THERMODYNAMIC EFFECTS OF FLUORINE AS A SUBSTITUENT IN ALKENES

BY

KARL S. MEDINGER

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1981

TO SELENA AND SUE-ELLEN

ACKNOWLEDGEMENTS

I would like to thank my research director, Dr. W. R. Dolbier, Jr., for the support and encouragement he has provided over the past five years. I am also grateful to Dr. B. E. Smart for a prepublication copy of his excellent review article, "Fluorocarbons," and to Dr. A. Greenberg for his communication on the incremental geminal fluorine stabilizations. Special thanks go to my family for their support and understanding during the long days and nights it took to accomplish my goals.

TABLE OF CONTENTS

PAGE

ACKNOWLEDGEMENTS iii

LIST OF TABLES vi

LIST OF FIGURES. vii

ABSTRACT ix

CHAPTERS

I INTRODUCTION 1

C-F Bonding. 2
Fluorine Effects on C-C Bonds. 4
Carbon-Carbon Double Bonds 5
Cis and Gauche Effects 7
Isomerizations Involving Fluorine. 7
Thermodynamic Preference of One Fluorine. 9
Thermodynamic Preference of Geminal Fluorines 11
Goals and Methods. 12

II RESULTS. 17

3-Fluoro-1,5-hexadiene 17
1,1-Difluoro-1,5-hexadiene 18
7,7-Difluoro-1,5-heptadiene. 19
7,7,7-Trifluoro-1,5-heptadiene 23
3-Fluoropropene. 25
Difluoropropene. 28

III DISCUSSION 31

IV EXPERIMENTAL 46

3-Fluoro-1,5-hexadiene, 16 47
Thermolysis of 16. 48
1,1-Difluoro-1,5-hexadiene, 17 48
3,3-Difluoro-1,5-hexadiene, 18 50

Thermolysis of 17 and 18 51
5,7-Dibromo-7,7-difluoro-1-heptene, 19. 52
7-Bromo-7,7-difluoro-1,5-heptadiene, 20t and 20c 53
7,7-Difluoro-1,5-heptadiene, 21c and 21t 54
3-Difluoromethyl-1,5-hexadiene, 22 55
Thermolysis of 22, 21c and 21t 56
5-Iodo-7,7,7-trifluoro-1-heptene, 23 . . . 56
7,7,7-Trifluoro-1,5-heptadiene, 24t and 24c 57
3-Trifluoromethyl-1,5-hexadiene, 25. . . . 59
Thermolysis of 24c, 24t and 25 59
3-Fluoropropene, 26. 60
1-Fluoropropene, 27c and 27t 60
Thermolysis of 26, 27c and 27t 61
3,3-Difluoropropene, 28. 62
1,1-Difluoropropene, 29. 62
Thermolysis of 28 and 29 63

APPENDICES

1 ^{1}H NMR, ^{19}F NMR, AND IR OF RELEVANT COMPOUNDS. 65

2 KINETIC AND THERMODYNAMIC DATA 98

REFERENCES 111

BIOGRAPHICAL SKETCH. 115

LIST OF TABLES

TABLE		PAGE
1	RATE DATA FOR 17 → 18	98
2	ARRHENIUS PARAMETERS FOR 17 → 18	102
3	EQUILIBRIUM CONSTANTS FOR 22 ⇌ 21c ⇌ 21t	103
4	ENTHALPY AND ENTROPY FOR 22 ⇌ 21c ⇌ 21t	104
5	EQUILIBRIUM CONSTANTS FOR 25 ⇌ 24c ⇌ 24t	105
6	ENTHALPY AND ENTROPY FOR 25 ⇌ 24c ⇌ 24t	106
7	EQUILIBRIUM CONSTANTS FOR 27c ⇌ 27t ⇌ 26	107
8	ENTHALPY AND ENTROPY FOR 27c ⇌ 27t ⇌ 26	108
9	EQUILIBRIUM CONSTANTS FOR 29 ⇌ 28	109
10	ENTHALPY AND ENTROPY FOR 29 ⇌ 28	110

LIST OF FIGURES

FIGURE		PAGE
1	^{19}F NMR of 3-Fluoro-1,5-hexadiene, 16, ϕ 177.6 ppm.	65
2	^{1}H NMR of 3-Fluoro-1,5-hexadiene, 16	66
3	IR of 3-Fluoro-1,5-hexadiene, 16	67
4	^{19}F NMR of 1,1-Difluoro-1,5-hexadiene, 17 ϕ 84.5 ppm	68
5	^{1}H NMR of 1,1-Difluoro-1,5-hexadiene, 17 . .	69
6	IR of 1,1-Difluoro-1,5-hexadiene, 17	70
7	^{19}F NMR of 3,3-Difluoro-1,5-hexadiene, 18, ϕ 97.9 ppm	71
8	^{1}H NMR of 3,3-Difluoro-1,5-hexadiene, 18 . .	72
9	IR of 3,3-Difluoro-1,5-hexadiene, 18	73
10	^{19}F NMR of 5,7-Dibromo-7,7-difluoro-1-heptene, 19, ϕ 43.3 ppm	74
11	^{1}H NMR of 5,7-Dibromo-7,7-difluoro-1-heptene, 19.	75
12	IR of 5,7-Dibromo-7,7-difluoro-1-heptene, 19.	76
13	^{19}F NMR of 7-Bromo-7,7-difluoro-1,5-heptadiene, 20c at ϕ 39.3 ppm.	77
14	^{1}H NMR of 7-Bromo-7,7-difluoro-1,5-heptadiene, 20c and 20t.	78
15	IR of 7-Bromo-7,7-difluoro-1,5-heptadiene, 20c and 20t.	79

16 ^{19}F NMR of 7,7-Difluoro-1,5-heptadiene, 21c at ϕ 111.4 ppm 80

17 ^{1}H NMR of 7,7-Difluoro-1,5-heptadiene, 21c and 21t. 81

18 IR of 7,7-Difluoro-1,5-heptadiene, 21c and 21t. 82

19 ^{19}F NMR of 3-Difluoromethyl-1,5-hexadiene, 22 83

20 ^{1}H NMR of 3-Difluoromethyl-1,5-hexadiene, 22 84

21 IR of 3-Difluoromethyl-1,5-hexadiene, 22 . . 85

22 ^{19}F NMR of 5-Iodo-7,7,7-trifluoro-1-heptene, 23, ϕ 64.4 ppm. 86

23 ^{1}H NMR of 5-Iodo-7,7,7-trifluoro-1-heptene, 23. 87

24 IR of 5-Iodo-7,7,7-trifluoro-1-heptene, 23 88

25 ^{19}F NMR of 7,7,7-Trifluoro-1,5-heptadiene, 24c at ϕ 58.9 ppm. 89

26 ^{1}H NMR of 7,7,7-Trifluoro-1,5-heptadiene, 24t and 24c. 90

27 IR of 7,7,7-Trifluoro-1,5-heptadiene, 24t and 24c. 91

28 ^{19}F NMR of 3-Trifluoro-1,5-hexadiene, 25, ϕ 71.5 ppm 92

29 ^{1}H NMR of 3-Trifluoro-1,5-hexadiene, 25. . . 93

30 IR of 3-Trifluoro-1,5-hexadiene, 25. 94

31 IR of 1-Fluoropropene, 27c and 27t 95

32 IR of 3,3-Difluoropropene, 28. 96

Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

THERMODYNAMIC EFFECTS OF FLUORINE AS A SUBSTITUENT IN ALKENES

By

Karl S. Medinger

December 1981

Chairman: William R. Dolbier, Jr.
Major Department: Chemistry

A limited amount of thermodynamic data has been published for fluorinated hydrocarbons and some of this contains a high degree of uncertainty. It is therefore difficult to make reasonable estimates of the heats of formation of even relatively simple fluorinated hydrocarbons. In this work, molecules which would provide relative thermodynamic data on specific effects of fluorine were synthesized and isomerized.

From the literature ΔH_f°'s for fluoroethane, and 1,1-difluoroethane, and 1,1,1-trifluoroethane, the following group values were estimated: $[C\text{-}H_2FC]$ = -52.7, $[C\text{-}HF_2C]$ = -108.6, and $[C\text{-}F_3C]$ = -167. These group values and the following Cope rearrangements, allow one to estimate

group values containing allylic fluorine. 3-Difluoro-1,5-hexadiene rearranged to cis-7,7-difluoro-1,5-heptadiene (ΔH = 0.563 kcal/mole) and to trans-7,7-difluoro-1,5-difluoro-1,5-heptadiene (ΔH = -0.80 kcal/mole). 3-Trifluoromethyl-1,5-hexadiene rearranged to cis-7,7,7-trifluoro-1,5-heptadiene (ΔH = 1.47 kcal/mole) and trans-7,7,7-trifluoro-1,5-heptadiene (ΔH = -0.23 kcal/mole). The following group values and cis corrections were estimated: $[C\text{-}H_2FC_D]$ = -52.2, $[C\text{-}HF_2C_D]$ = -107.6, $[C\text{-}F_3C_D]$ = -166.0, cis correction (CHF_2 cis to CH_2) = 1.37, and cis correction (CF_3 cis to CH_2) = 1.63

From the above group values and the iodine catalyzed isomerization of 3-fluoropropene and 3,3-difluoropropene, one can estimate the group values for vinylic fluorines. 3-Fluoropropene was isomerized to trans-1-fluoropropene (ΔH = -2.68 kcal/mole) and to cis-1-fluoropropene (ΔH = -3.34 kcal/mole). 3,3-Difluoropropene was isomerized to 1,1-difluoropropene (ΔH = 2.5 kcal/mole). The following group values and cis corrections were estimated: $[C_D\text{-}HF]$ = -38.4, $[C_D\text{-}F_2]$ = -88.0, and cis correction (F cis to CH_3) = -0.64.

The Cope rearrangement of 1,1-difluoro-1,5-hexadiene to 3,3-difluoro-1,5-hexadiene yielded the following kinetic parameters: E_a = 33.0 kcal/mole, log A = 10.8 sec^{-1}, and $S^{\ddagger}$ = -12.2 e.u. ΔH for this reaction was

estimated to be -5.1 kcal/mole and the following group values were estimated: $[C\text{-}F_2CC_D]$ = -103.9 and $[C\text{-}F_2C_2]$ = -104.9.

CHAPTER I
INTRODUCTION

Fluorine produces some unique effects when it is used as a substituent in hydrocarbon systems. These effects arise from three factors. Fluorine is a second period element, fluorine is the most electronegative of the elements, and fluorine has three pairs of nonbonding electrons. The interaction of these three factors is demonstrated by fluorine's effects upon reaction intermediates.

The electronegativity of fluorine gives rise to inductive electron withdrawal towards fluorine and away from carbon. Fluorine substitution beta to a carbanion is stabilizing and fluorine substitution beta to a carbonium ion is destabilizing.[1]

Fluorine bound directly to a carbonium ion destabilizes the electron deficient center by inductive effects. However, fluorine also uses its nonbonding electrons to stabilize the carbonium ion by resonance. The resonance effect predominates, with the net effect being stabilization.[1]

$$C^{+} \longrightarrow F \longleftrightarrow C \equiv F^{+}$$

When fluorine is attached to a carbanion, the sigma withdrawing effect is stabilizing. But electron repulsions between filled p orbitals on fluorine and carbon are destabilizing. Depending upon the geometry of the system, fluorine can be either mildly stabilizing or destabilizing.[1]

$$C^{-} \longrightarrow F$$

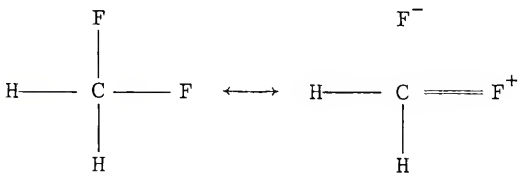
C-F Bonding

The bonding between carbon and fluorine changes as the number of fluorines bonded to the same carbon increases. Upon successive fluorination, the C-F bond is shortened and becomes stronger. In addition, the ΔH_f° is also lowered.

	r(C-F) Å[2]	D (C-F) kcal/mole[3]	ΔH_f° kcal/mole[4]
CH_3F	1.385	108.8	-55.9
CH_2F_2	1.358	122.0	-108.9
CHF_3	1.332	128.0	-167.0
CF_4	1.317	129.7	-223.4

Several explanations for this effect have been proposed, all of which use systematic changes in the bonding to explain these effects. Pauling proposed double-bond no-bond resonance structures to account for the shortening

and increased strength of the C-F bonds.[5] For fluoromethane, no double-bond no-bond resonance structure would exist. Therefore, its C-F bond distance would be the longest. Upon successive fluorination, more resonance structures can be drawn and the C-F bond distance should decrease. Ab initio calculations (4-31G) support this description. In a molecular orbital approach a p orbital on fluorine is mixed with an acceptor sigma C-F bond.[6,7]



Bent[8] and Bernett[9] use a hybridized atomic orbital scheme to explain the C-F bonding. Since the fluorine is very electronegative, the carbon atom uses more p character in the C-F bond. As more fluorines are bound to the same carbon, there would be less p character available for each fluorine. The p character in the C-F bond increases in the series CH_3 ($sp^{3.25}$), CH_2F_2 ($sp^{3.18}$), CHF_3 ($sp^{3.10}$) and CF_4 (sp^3).[9] This approach also explains the bond angles in difluoromethane, ∠FCF (108.3°) and ∠HCH (111.9°).[9] As the p character of the C-F bond is increased, the angle between the fluorines will shrink.

Since the C-H bonds contain more s character, the angle between the hydrogens should increase.

Fluorine Effects on C-C Bonds

Fluorination changes the strength of C-C bonds. The dissociation energy of the C-C bond in ethane is 88.4 kcal/mole, for hexafluoroethane is 98.4 kcal/mole, and for 1,1,1-trifluoroethane is 101.2 kcal/mole.[10] The fluorines strengthen the C-C bond by 10 kcal/mole and 12.8 kcal/mole, respectively.

The bond strengthening effects of fluorine are seen in the pyrolysis of fluorinated cyclobutanes. The activation energy for this process involves breaking two carbon-carbon bonds. Upon increased fluorine content the activation energy increased.

	log A(sec^{-1})	E_a(kcal/mole)	ref.
$\rightarrow 2\ H_2C{=}CH_2$	15.6	62.5	11
$\rightarrow H_2C{=}CH_2 + H_2C{=}CF_2$	15.61	67.2	12
$\rightarrow 2\ H_2C{=}CF_2$	15.35	69.8	13
$\rightarrow H_2C{=}CH_2 + F_2C{=}CF_2$	15.27	73.6	13
$\rightarrow 2\ F_2C{=}CF_2$	15.97	74.2	14

Carbon-Carbon Double Bonds

Carbon-carbon double bonds undergo a contraction in length upon successive fluorination. The addition of the first fluorine has little effect on the carbon-carbon bond length. However, for 1,1-difluoroethene, there is a pi bond shortening of 0.018 Å. An interesting feature of this molecule, and tetrafluoroethene, is the FCF bond angle. Bernett[9] rationalized this effect by invoking hybridization effects. The C-F bonds are essentially sp^3 hybridized. This leaves an sp orbital for the sigma bond and a p orbital for the pi bond.

	$H_2C{=}CH_2$ [15]	$HFC{=}CH_2$ [16]	$F_2C{=}CH_2$ [17]	$F_2C{=}CF_2$ [18]
r(C-C) Å	1.337	1.333	1.315	1.311
r(C-F) Å		1.348	1.323	1.319
∠HCH	120.8°	120.4°	121.8°	
∠HCF		115.4°		
∠FCF			109.3°	112.5°

From the distortions produced by the fluorines one would expect that the double bond would be weakened. Pickard and Rodgers[19] using D°_{π} $(H_2C{=}CH_2){=}DH^{\circ}_f(CH_3CH_2\text{-}H)\text{-}DH^{\circ}_f(\cdot CH_2CH_2\text{-}H)$, calculated the pi dissociation energy for tetrafluoroethene (52.5 kcal/mole), 1,1-difluoroethene (62.5 kcal/mole), and ethene (59.0 kcal/mole), difluoroethene being 3.5 kcal/mole more stable than ethene. However, the hydrogenation

of difluoroethene is 4 kcal/mole more exothermic than ethylene.[20] So even though the pi bond is not destabilized by the geminal fluorines, there is a thermodynamic advantage for the saturated fluorocarbon system over the hydrocarbon system.

	I.P.(eV)	Ref.
$H_2C=CH_2$	10.51	21
$H_2C=CHF$	10.56	21
$H_2C=CF_2$	10.69	21
$F_2C=CF_2$	10.56	21
$CH_3CH=CH_2$	9.86	22
$FCH_2CH=CH_2$	10.60	23

Photoelectron spectrums for few fluorocarbons have been determined. The effect of one or two fluorines on a pi molecular orbital is not large. Vinylic fluorine is both a sigma withdrawer, which lowers both sigma and pi molecular orbitals, and a pi donator, which raises the pi energy level. Vinylic fluorine has a small effect on the pi orbitals and a large effect on the sigma orbitals. This has been termed the perfluoro effect.[24] The effect of one allylic fluorine is much more dramatic, 18 times the magnitude of the effect of one vinylic fluorine.

Cis and Gauche Effects

In 1-fluoropropane, the gauche conformation is favored by 0.47 kcal/mole over the trans conformation.[25] The same type of effect is seen for 1-fluoropropene, where the cis isomer is 0.75 kcal/mole more stable than the trans isomer.[26] A. Liberles, A. Greenberg, and J. E. Eilers discuss these effects in terms of bonding between the methyl and fluorine.[27]

R. C. Bingham proposed conjugative destabilization effects to explain the cis and gauche effects.[28] His reasoning follows. Electrons delocalize preferentially in straight lines. Therefore, two substituents interact stronger when they are trans to each other. For 1-fluoropropene, the fluorine is a pi donor. If the methyl group had an acceptor orbital to interact with the pi bond, then the trans isomer would be stabilized relative to the cis isomer. However, since the methyl group has no suitable acceptor component, then the situation is governed by filled orbital-orbital interactions. The cis isomer minimizes these destabilizations. The author uses an analogous explanation to explain the gauche effect.

Isomerizations Involving Fluorine

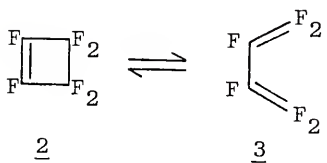
The classic experiment demonstrating the unusual effects of fluorine was the thermolysis of perfluorocyclobutene, 2. When cyclobutene, 1, was heated it opened

quantitatively to 1,3-butadiene. The ΔH for this reaction was calculated from standard heats of formation.[29]

ΔH = -8 kcal/mole

1

When 2 was heated, E. W. Schalag and W. B. Peatman found that the cyclic compound was now enthalpicly favored over the open form, 3.[30] The enthalpic difference between the two reactions is 20 kcal/mole. The authors cited two possible major driving forces involved in this equilibrium. One, the transformation of two sp^2 hybridized



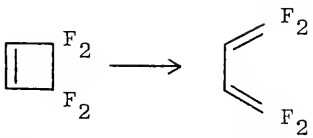
ΔH = 11.7 kcal/mole

2 3

difluoromethylene groups to sp^3 hybridized and two, the transformation of two $-CF=CF_2$ units into a more stable saturated situation.

H. M. Frey, R. G. Hopkins, and I. C. Vinall studied the opening of 3,3,4,4-tetrafluorocyclobutene, 4 to 1,1,4,4-tetrafluoro-1,3-butadiene, 5.[31] 4 opens to 5

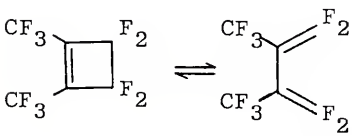
with no detectable amount of 4 left.



4 5

If the rehybridization of the two difluoromethylene groups was the major driving force, then the ΔH for 4 → 5 should have been very similar to the ΔH for 2 → 3. This was not the case. The two fluorines in the one and two positions on 3 exert a large effect on the relative stabilities of the closed and open compounds. Therefore, the major driving force in the closure of 3 to 2 was the elimination of the two highly destabilized $-CF=CF_2$ units.[9]

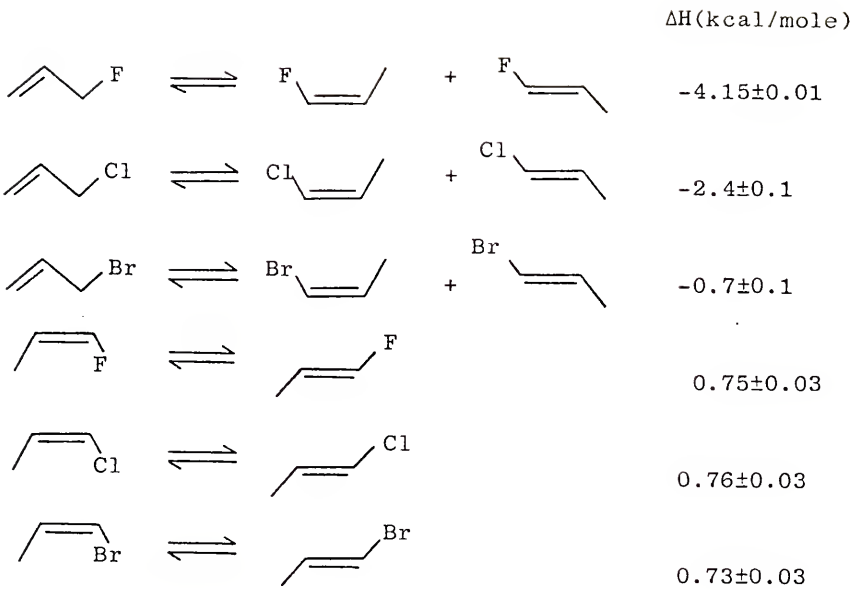
J. P. Chesick studied the equilibrium involving decafluoro-1,2-dimethylcyclobutene, 6, and decafluoro-2,3-dimethyl-1,3-butadiene, 7.[29] The trifluoromethyl substituent destabilizes the carbon-carbon double bond as does fluorine, but to a lesser extent.



ΔH = 0.4 kcal/mole

Thermodynamic Preference of One Fluorine

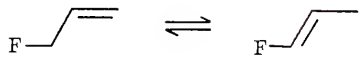
Paul I. Abell and Paul K. Adolf isomerized allyl halides with hydrogen bromide and light.[26]



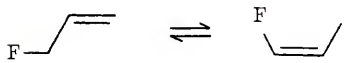
For all three halogens, the vinylic isomer was found to be more stable. This is quite a contrast to the fluorinated cyclobutene-butadiene systems in which fluorine prefers to be on an sp^3 hybridized carbon. In addition for the vinyl halogens, the cis isomer was found to be more stable than the trans form, an example of the cis effect.

In 1973, in a paper on the iodine catalyzed isomerization of allyl chloride,[32] Alfassi, Golden and Benson commented that the enthalpy and entropy values obtained by Abell and Adolf were high. From the heats of formation of 1-fluoropropene and 3-fluoropropene, Alfassi, Golden and Benson

calculated enthalpy values for the isomerizations listed below.



$\Delta H = -2.2 \pm 0.4$ kcal/mole

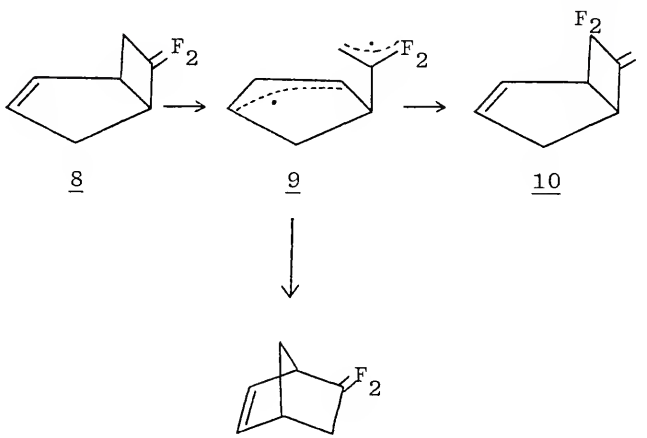


$\Delta H = -2.9 \pm 0.5$ kcal/mole

Thermodynamic Preference of Geminal Fluorines

The thermodynamic preference of geminal fluorines is not as well verified as the effect of a single fluorine. 4 opens quantitatively to 5 when heated.[31] Since no equilibrium was observed, no information about geminal substitution was obtained.

Another isomerization involving geminal fluorines was the thermolysis of 6-difluoromethylenebicyclo(3.2.0)heptene 8.[33]

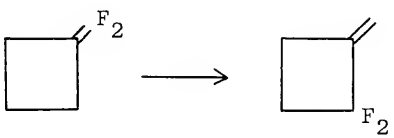


8 9 10

11

8 opens to diradical 9. Closure to 11 relieves 13.5 kcal/mole of strain energy and was the major closure pathway. However, 9 can close to 10, where the geminal fluorines are now allylic.

Another isomerization involving changing a vinyl difluoromethylene group to an allylic position was the thermolysis of difluoromethylenecyclobutane, 12.[34] 12 rearranges to 13 with no observable equilibrium. Once again, the geminal fluorines prefer to be allylic rather than vinylic.



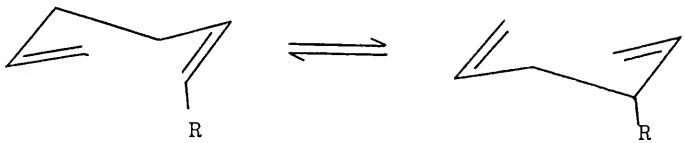
12 13

From the preceding discussion it is obvious that there is a real need for further study of the effects of geminal fluorines since there exists no quantitative work on this subject.

Goals and Methods

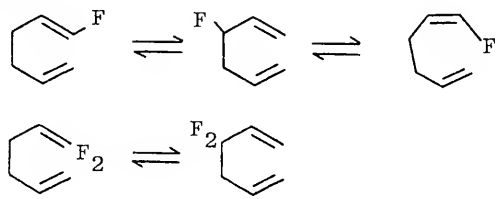
The object of this work is to design, synthesize and isomerize appropriately fluorinated molecules that will yield information about the thermodynamic preference of fluorine. The two systems used are Cope reactions and iodine catalyzed propene isomerizations.

The Cope rearrangement of 1,5-hexadienes has been established to proceed by a unimolecular route. The transition state involves a six-membered chair conformation.[35] These reactions typically have

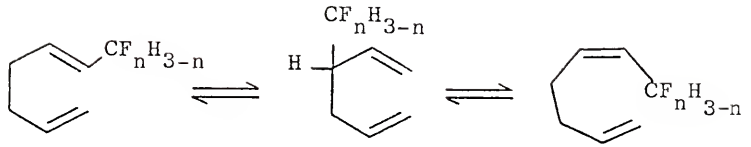


an activation energy in the range of 25-35 kcal/mole.[36] Since this is a comparably low activation energy process, the number of annoying side reactions should be limited, especially the loss of hydrogen fluoride.

Reactions of interest are those that change a carbon, to which one or two fluorines are bound, from sp^2 to sp^3 hybridization.

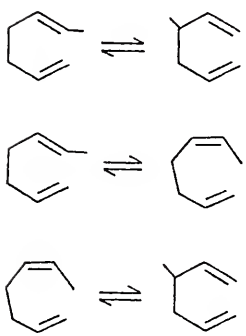


Also of importance would be equilibria involving substituents that change from allylic to alkyl. These equilibria can be directly



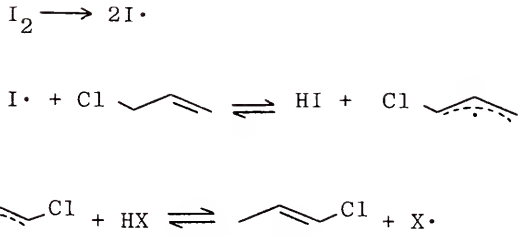
n = 1,2,3

compared to the work of H. M. Frey and R. K. Solly, who measured the entropy for the 1,5-heptadiene to 3-methyl-1,5-hexadiene equilibrium.[35]

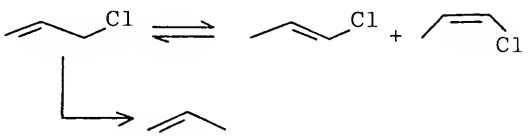


ΔH(kcal/mole)	ΔS(e.u.)
1.28 ± 0.06	-0.51 ± 0.06
0.51 ± 0.03	-0.60 ± 0.06
0.76 ± 0.05	0.07 ± 0.09

The second series of equilibria pertinent to this study would be the iodine catalyzed propene isomerizations. This method was used for the isomerization of butene[37] and chloropropene.[32] The mechanism that was proposed is outlined below, where HX is chloropropene or hydrogen iodide.

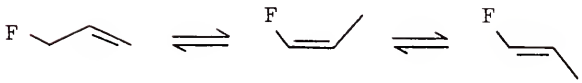


The major side product was the loss of chlorine to form propene. When the rate of propene formation was competitive with the allyl isomerization, the equilibrium constant measured would not have been the correct value. However, the authors noted that as the temperature



was increased, the rate of propene formation decreased relative to the rate of isomerization reactions. Therefore, the utility of this reaction lies in the temperature range of approximately 300° to 400°.

Systems relevant to this work would be the iodine catalyzed isomerization to fluoropropene and 1,1-difluoropropene.



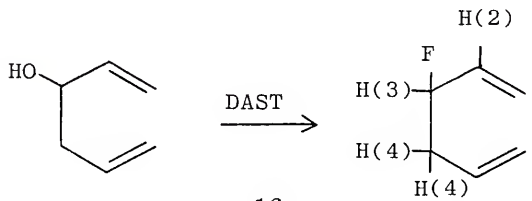
$$CF_2H\text{-}CH{=}CH_2 \rightleftharpoons CF_2{=}CH\text{-}CH_3$$

CHAPTER II
RESULTS

All of the compounds which are discussed in this section, unless otherwise noted, have not heretofore been mentioned in the literature.

3-Fluoro-1,5-hexadiene

3-Fluoro-1,5-hexadiene, 16, was synthesized in a one step process with a yield of 25%, from 1,5-hexadien-3-ol. Diethylaminosulfur trifluoride (DAST) replaced the -OH with a single fluorine.[38]



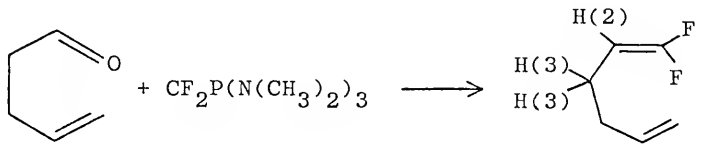
16

The two bond HF coupling was 48 Hz (figure 1). The fluorine was also split by H(4) and H(2), along with some longer range minor coupling. Only the upfield leg of the signal for H(3) was visible as a quartet (figure 2). The downfield leg was buried in the vinyl region. ^{1}H NMR and IR (figure 3) both confirm the presence of the terminal double bonds.

Thermolysis of 16 at 160° resulted in its conversion to 1,3,5-hexatriene, by loss of hydrogen fluoride. The 1,3,5-hexatriene was also in equilibrium with 1,3-cyclohexadiene.

1,1-Difluoro-1,5-hexadiene

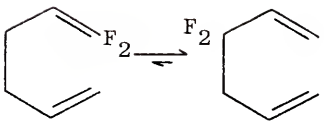
1,1-Difluoro-1,5-hexadiene, 17 was prepared in a 9.5% yield from 4-pentenal[39] via the Wittig-type procedure of Naae and Burton.[40]



17

The geminal fluorines in 17 appeared in the ^{19}F NMR (figure 4) as an ABX pattern. The trans HF coupling was 20 Hz and the cis HF coupling was less than 1 Hz. H(2) was shifted upfield 1 ppm by the trans fluorine (figure 5). H(2) appeared as a doublet of a triplet. This was further split by the cis fluorine. Both ^1H NMR and IR (figure 6) showed the presence of a terminal double bond. Also seen in the IR was the strong $C=CF_2$ absorption at 1750 cm^{-1}.

When 17 was heated it rearranged to 3,3-difluoro-1,5-hexadiene, 18, which was identified by its IR (figure 9), ^{19}F NMR (figure 7), ^1H NMR (figure 8), and mass spectrum.



17 18

The geminal fluorines in 18 occurred in the ^{19}F NMR as a triplet, that was doubled by a three bond coupling to the vinylic hydrogen. The IR spectrum exhibited an absorbance due to the terminal vinyl groups at 1650 cm^{-1}.

Thermolysis of 17 at six different temperatures between 194.3° and 214.6° generates the data presented in table 1 and the rate constants listed below and in table 2. At 194.3°, due to the slow rate of isomerization of 17 to 18, the equilibrium had not been reached. Therefore excluding the data at 194.3°, a ΔG_{avg} of -5.1 ± 0.3 kcal/mole was calculated at an average temperature of 206.6°.

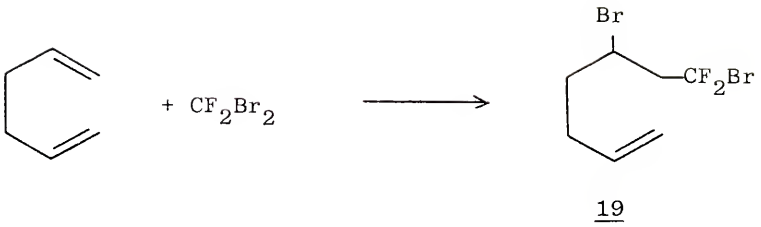
E_a = 33.0 ± 0.7 kcal/mole

log A = 10.8 ± 0.3 sec^{-1}

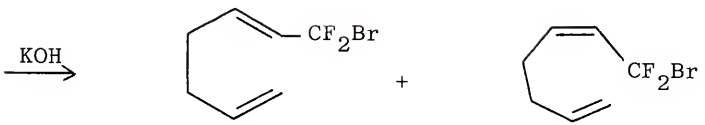
$\Delta S^{\ddagger}$ = -12.2 e.u.

7,7-Difluoro-1,5-heptadiene

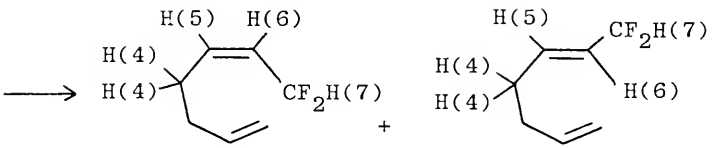
7,7-Difluoro-1,5-heptadiene, 21, was synthesized by the following route.



19



20t 20c

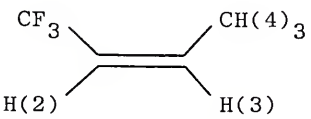


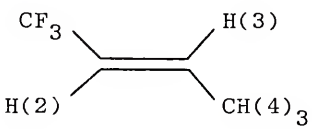
21c 21t

Radical addition of difluorodibromomethane to hexadiene yielded 5,7-dibromo-7,7-difluoroheptene, 19, in 27% yield. IR (figure 12) and ^1H NMR (figure 11) show the presence of a terminal vinyl group. A triplet in the ^{19}F NMR (figure 10) confirms the orientation of the radical addition.

Dehydrohalogenation of 19 with potassium hydroxide afforded 7-bromo-7,7-difluoro-1,5-heptadiene, 20, in 77% yield. Integration of the ^{19}F NMR (figure 13) yielded a cis to trans ratio of 5:95.

Tri-n-butyltin hydride[41] replaced the bromine in 20 with a hydrogen to yield 21 in 42% yield. The IR (figure 18) exhibited both an internal and an external double bond stretch. In the ^{1}H NMR (figure 17), a doublet was seen at 6.95 ppm, which is one leg of the signal for H(7). The remaining two legs were buried in the vinyl region. The fluorines in 21c and 21t were split by a geminal H(7)F coupling of 56.0 Hz and 59.5 Hz (figure 16), respectively. Further splitting enables one to assign the geometry about the double bond. Haszeldine reported the coupling constants for 1,1,1-trifluoro-2-butene.[42] For 21c, one would

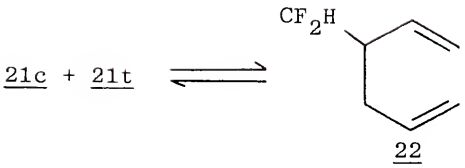




$J_{FH(2)}$ = 8.5 Hz
$J_{FH(3)}$ = 0 Hz
$J_{FH(4)}$ = 2.8 Hz

$J_{FH(2)}$ = 6 Hz
$J_{FH(3)}$ = 2.6 Hz
$J_{FH(4)}$ = 2.1 Hz

expect a $J_{FH(6)}$ of about 8 Hz and each resulting leg would be split into a triplet by the two H(4)'s. This corresponds to the absorption at 111.4 ppm. For 21t, $J_{FH(6)}$ was expected to be about 6 Hz. If $J_{FH(5)}$ and $J_{FH(4)}$ were both about 2 Hz, then one would expect to see two multiplets for 21t. These multiplets occur at 110.3 ppm.



Heating 21c and 21t resulted in an equilibrium mixture of 21c, 21t, and 3-difluoromethyl-1,5-hexadiene, 22. Collection of several runs and preparative glpc afforded 22, which was used without further purification. The IR spectrum (figure 21) for 22 exhibited an absorbance for a terminal vinyl group at 1645 cm^{-1} and no internal double bond stretch. The geminal HF coupling was 56.7 Hz and the three bond HF coupling was 15.1 Hz (figure 18).

22 was pyrolyzed at nine different temperatures between 309.9° and 409.0°. At 409.0°, the equilibrium was established from either a mixture of 21c and 21t or 22. Table 3 contains the equilibrium constants and table 4 contains the results of the van't Hoff plots, which are also listed below.

21c $\rightleftharpoons$ 22

$\Delta H = -0.563 \pm 0.006$ kcal/mole

$\Delta S = 0.733 \pm 0.002$ e.u.

21t $\rightleftharpoons$ 22

$\Delta H = 0.80 \pm 0.04$ kcal/mole

$\Delta S = -0.36 \pm 0.02$ e.u.

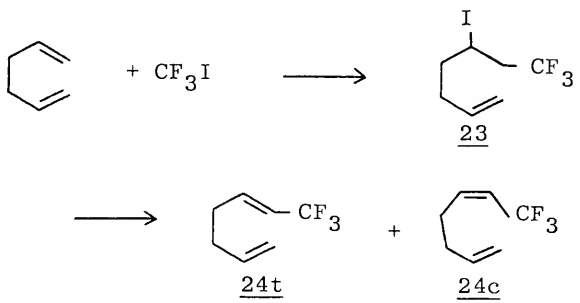
21t $\rightleftharpoons$ 21c

$\Delta H = 1.37 \pm 0.04$ kcal/mole

$\Delta S = -1.09 \pm 0.01$ e.u.

7,7,7-Trifluoro-1,5-heptadiene

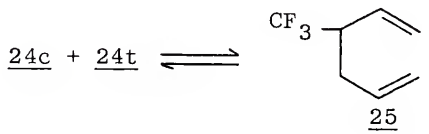
7,7,7-Trifluoro-1,5-heptadiene, 24, was synthesized by a modification of the procedure used by Haszeldine to synthesize 1,1,1-trifluoro-2-butene.[42]



Radical addition of trifluoromethyl iodide to hexadiene afforded 5-iodo-7,7,7-trifluoro-1-heptene, 23, in 60% yield. Both IR (figure 24) and ^1H NMR (figure 23) show the presence of a terminal vinyl group. The three fluorines appeared as triplet in the ^{19}F NMR (figure 22).

Dehydrohalogenation of 23 afforded 24c and 24t, in 47% yield. Assignment of cis and trans was done by

analogy to the previously discussed compound, 21. Integration of the ^{19}F NMR yields a cis to trans ratio of 13:87 (figure 25). In the IR (figure 27), there were absorptions due to the internal and external double bonds.



Thermolysis of the synthetic mixture of 24c and 24t gave rise to an equilibrium mixture containing starting materials plus 3-trifluoromethyl-1,5-hexadiene, 25. Several runs were combined and 25 was isolated by preparative glpc. 25 exhibited a vinyl stretch at 1650 cm^{-1} in the IR (figure 30). In the ^{19}F NMR (figure 28), the three fluorines appeared as a doublet, with a three bond HF coupling of 8.7 Hz.

25 was pyrolyzed at eight temperatures between 321.3° and 408.0°. The equilibrium at 408.0° was established from either 25 or the mixture of 24c and 24t. The resulting equilibrium constants are listed in table 5, and the results from the van't Hoff plots are listed in table 6 and are repeated below.

24c $\rightleftharpoons$ 25

$\Delta H = -1.47 \pm 0.07$ kcal/mole

$\Delta S = -0.51 \pm 0.02$ e.u.

24t $\rightleftharpoons$ 25

$\Delta H = 0.23 \pm 0.05$ kcal/mole

$\Delta S = -1.52 \pm 0.02$ e.u.

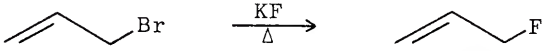
24t $\rightleftharpoons$ 24c

$\Delta H = 1.63 \pm 0.08$ kcal/mole

$\Delta S = -1.12 \pm 0.02$ e.u.

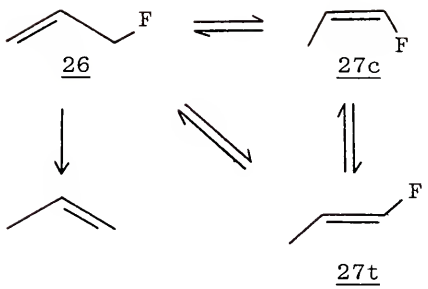
3-Fluoropropene

3-Fluoropropene, 26, was made by the method of Hoffman.[43] The ^{1}H NMR[44], IR[45], and ^{19}F NMR[44] were consistent with the data published in the literature.



26

When 26 was heated in the presence of a catalytic amount of iodine, three products appeared in the glpc. The product with the shortest retention time, propene, was identified by glpc comparison with an authentic sample. The remaining two products, cis-1-fluoropropene, 27c, and trans-1-fluoropropene, 27t, were collected and identified. The ^{1}H NMR and ^{19}F NMR were consistent with the literature data.[46]



26 27c 27t

This isomerization probably follows a radical chain process, as proposed by S. W. Benson for the iodine catalyzed isomerization of chloropropene.[32] Thermolysis of the iodine yields iodine atoms, which can then abstract an allylic hydrogen from fluoropropene. In the chain propagating step, the allylic radical abstracts a hydrogen atom from fluoropropene. The proposed mechanism for the formation of propene was the attack of the iodine atom on the chlorine[32] or, in this case, the attack on the fluorine.

One problem inherent in this reaction was the introduction of the iodine into the pyrolysis vessel. The iodine was expanded from a glass storage vessel into the pyrolysis vessel and the excess iodine was recondensed back into the storage bulb. The amount of iodine lost was determined by the difference in weight of the storage vessel. Quantitatively, this method was not accurate for the following reasons. The iodine would condense on the

coolest parts of the vacuum line, the teflon stopcocks. This caused difficulties in recondensing all of the iodine. Another problem was the solubility of the iodine in the stopcock grease, which was used in the glass joints. Due to these difficulties, it was not possible to assess the amount of iodine present in the pyrolysis vessel. Further, in each run the amount of iodine added could not be reproduced.

In each pyrolysis, the rate of propene formation was different due to the differing concentrations of fluoropropene and iodine. Also, in each run, the measured equilibrium constants were found to be invariable over the entire sampling time, no matter how much propene was present in the reaction mixture. Acceptable equilibrium constants were measured for runs with as little as 3% propene and for runs with as much as 25% propene. At 312°, the bleed off to propene occurred at a sufficient rate to effect the measured equilibrium constants. In four separate runs at this temperature, $K_{\underline{27t}/\underline{26}}$ varied from 4.60 to 5.29 or 14% and $K_{\underline{27c}/\underline{26}}$ varied from 8.83 to 10.2 or 15% (table 7). At 343.9°, the lowest temperature used in the van't Hoff plots, $K_{\underline{27t}/\underline{26}}$ varied 2% and $K_{\underline{27c}/\underline{26}}$ varied 3%. At 356.0°, the deviation among the four runs was 1% for $K_{\underline{27t}/\underline{26}}$ and 2% for $K_{\underline{27c}/\underline{26}}$, which fell within the experimental error of the integrator.

26 was isomerized with iodine at six temperatures between 343.9° and 430.3°. At 430.3°, the equilibrium was established from 26 and the mixture of 27c and 27t. The resulting equilibrium values are listed in table 7 and the results of the van't Hoff plots are listed below and in table 8.

27t $\rightleftharpoons$ 27c

$\Delta H = -0.64 \pm 0.09$ kcal/mole

$\Delta S = 0.30 \pm 0.03$ e.u.

26 $\rightleftharpoons$ 27c

$\Delta H = -3.34 \pm 0.07$ kcal/mole

$\Delta S = -1.39 \pm 0.02$ e.u.

26 $\rightleftharpoons$ 27t

$\Delta H = -2.68 \pm 0.07$ kcal/mole

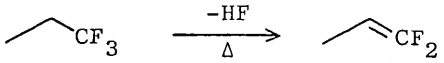
$\Delta S = -1.70 \pm 0.02$ e.u.

Difluoropropene

The ^{1}H NMR and ^{19}F NMR for 3,3-difluoropropene, 28, have been reported in the literature.[44] However, its synthesis has not been reported. 28 was synthesized, in 34% yield, in a one-step procedure from acrolein. DAST replaced the carbonyl oxygen with two fluorines.[38]

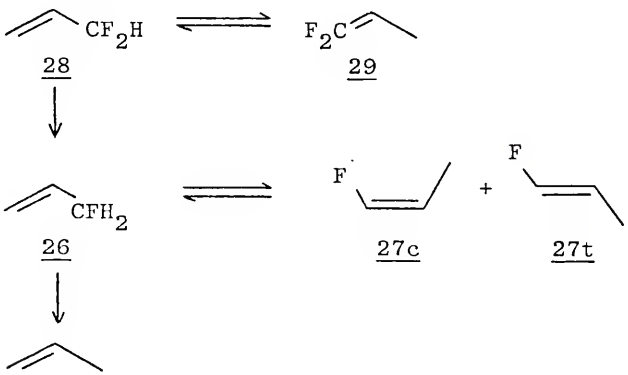
28

1,1-Difluoropropene, 29, was prepared by the procedure of S. J. Moss and K. R. Jennings.[47] 1,1,1-Trifluoropropane was dehydrohalogenated at 700° to produce 29 in 7.5% yield, whose ^{1}H NMR, ^{19}F NMR, and IR matched the data published in the literature.[48]



29

Iodine catalyzed isomerization of 28 resulted in an equilibrium mixture of 28 and 29, along with small amounts of 27c, 27t, and 26. With long reaction times, a small amount of propene was also formed.



28 29 26 27c 27t

Isomerization of 28 with iodine was accomplished at six temperatures between 378.3° and 412.8° and the resulting data are listed in table 9. Starting with 28 or 29, the equilibrium at 412.8° was established. The results from the van't Hoff plot of the data are presented below and in table 10.

$$29 \rightleftharpoons 28$$

$$\Delta H = -2.5 \pm 0.1 \text{ kcal/mole}$$

$$\Delta S = -0.38 \pm 0.04 \text{ e.u.}$$

CHAPTER III
DISCUSSION

Using S. W. Benson's empirical method for estimating thermochemical data, the heat of formation of a compound can be treated as the sum of all the groups contained in the molecule, plus any corrections for ring strain, cis effects, gauche effects, etc.[49] A group is defined as a polyvalent atom, along with its ligands. When defining the group, the polyvalent atom is always listed first, followed by its ligands. Therefore, the group [C-H_3C] represents a carbon with three hydrogen and one carbon ligand.[49]

Reliable group values for groups which contain only hydrogen and carbon have been derived empirically using thermochemical data from the literature.[49] The implicit error limits for a heat of formation estimation is ± 0.5 kcal/mole. From the heat of formation of fluoroethane,[50] 1,1-difluoroethane,[51] and 1,1,1-trifluoroethane,[51] the fluoroalkyl group values may be estimated (equations 1, 2 and 3).

$\Delta H_f^\circ(CH_3CH_2F)$ = [C-H_3C] + [C-H_2FC] = -62.9 kcal/mole

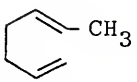
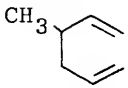
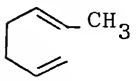
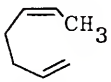
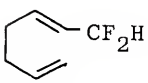
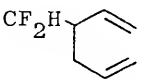
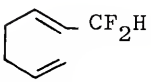
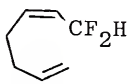
[C-H_3C] = -10.20

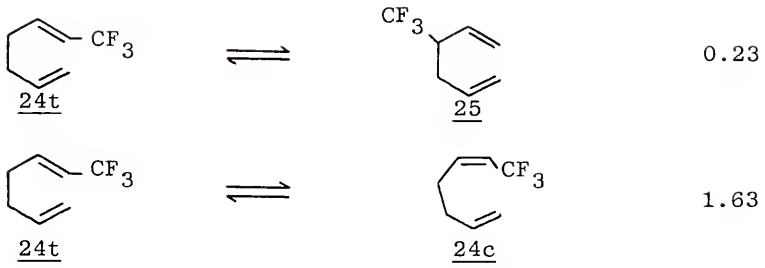
$[C\text{-}H_2FC] = -52.7$ 1

$\Delta H_f^\circ(CH_3CHF_2) = [C\text{-}H_3C] + [C\text{-}HF_2C] = -118.8$ kcal/mole
$[C\text{-}HF_2C] = -108.6$ 2

$\Delta H_f^\circ(CH_3CF_3) = [C\text{-}H_3C] + [C\text{-}F_3C] = -178.0$ kcal/mole
$[C\text{-}F_3C] = -167.8$ 3

One can use the thermochemical data from the equilibria listed below to estimate the group values for allylic groups with one, two, or three fluorines.

	ΔH(kcal/mole)
 14t ⇌  15	+1.28[35]
 14t ⇌  14c	0.51[35]
 21t ⇌  22	0.80
 21t ⇌  21c	1.37



For 15, 22, and 25 a gauche correction must be estimated due to the steric interactions between carbons three and four. The gauche correction for 15 is estimated from the experimental $\Delta H(14t \rightleftharpoons 15)$ (equation 4). From the equilibrium involving 14t and 14c, the cis correction is estimated (equation 5).

gauche corr. (15) = 0.33 4

cis corr. (CH_3 cis to CH_2) = 0.51 5

Assuming a correlation between the cis and gauche effects allows one to estimate a gauche correction for 22 and 25. Equations 6 and 7 give the cis corrections for difluoromethyl and trifluoromethyl substituents.

cis corr. (CHF_2 cis to CH_2) = 1.37 6

cis corr. (CF_3 cis to CH_2) = 1.63 7

The cis corrections for the difluoromethyl-methylene interaction and the trifluoromethyl-methylene interaction

are 2.7 and 3.2 times greater than the cis corrections for a methyl-methylene interaction, respectively. Therefore, the gauche corrections for 22 and 25 may be considered to be 2.7 and 3.2 times the gauche correction for 15 (equations 8 and 9).

$$\text{gauche corr. } (\underline{22}) = 0.89 \qquad 8$$

$$\text{gauche corr. } (\underline{25}) = 1.05 \qquad 9$$

The group values for two or three allylic fluorines may now be estimated from the enthalpy differences for the reactions 21t $\rightleftharpoons$ 22 and 24t $\rightleftharpoons$ 25 and the appropriate gauche corrections.

$$[C\text{-}HF_2C_D] = -107.6 \qquad 10$$

$$[C\text{-}F_3C_D] = -166.0 \qquad 11$$

The difference between the alkyl and allylic group values is the destabilization produced by the allylic fluorines. For difluoromethyl, the destabilization is 1 or 0.5 per fluorine. For trifluoromethyl, the effect is 1.8 or 0.6 per fluorine. Therefore, assuming that the effect of one fluorine is 0.5, the group value for a single allylic fluorine can be calculated (equation 12).

$$[C\text{-}H_2FC_D] = -52.2 \qquad 12$$

From $\Delta H(\underline{26} \rightleftharpoons \underline{27t})$ and equation 12, the group value for one vinylic fluorine substituent may be estimated (equation 13).

$CH_2{=}CHCH_2F \rightleftharpoons CH_3CH{=}CHF \qquad \Delta H = -2.68$ kcal/mole

<u>26</u> <u>27t</u>

$[C_D\text{-}HF] = -38.4$ 13

The cis isomer, <u>27c</u>, is thermodynamically more stable than the trans isomer, <u>27t</u>. Therefore, the cis correction is negative (equation 14).

cis corr. (F cis to CH_3) = -0.64 14

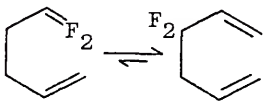
Using $\Delta H(\underline{28} \rightleftharpoons \underline{29})$, the group value for geminal vinylic fluorines may be estimated (equation 15). In this calculation, the cis correction for <u>29</u> and <u>27c</u> is assumed to be the same.

$CH_2{=}CHCHF_2 \rightleftharpoons CH_3CH{=}CF_2 \qquad \Delta H = 2.5$ kcal/mole

<u>28</u> <u>29</u>

$[C_D\text{-}F_2] = -88.0$ 15

The group value [C-F_2CC_D] can be estimated from the equilibrium involving 17 and 18. This system was too one-sided to obtain a good van't Hoff plot. An average ΔG of 5.1 ± 0.3 kcal/mole was found at an average temperature of 206.6°. The geminal fluorines had very little entropic effect (ΔS = 0.38 e.u.) on the equilibrium involving 28 and 29. Entropy effects in a substituted hexadiene system are considerably less important than the entropy effects in an equivalently substituted propene system. Therefore, a reasonable estimate for the entropy is 0.0 ± 0.5 e.u. For 17 $\rightleftharpoons$ 18 an enthalpy of 5.1 ± 0.6 kcal/mole is calculated.



17 18

ΔH = -5.1 ± 0.6 kcal/mole

Using the previously stated assumption that the gauche and cis effects are related, allows one to estimate a gauche correction for 18. The cis correction for a fluorine-methyl interaction is -1.3 times larger than a methyl-methylene cis interaction, where the negative sign represents a stabilizing fluorine-methyl interaction. Therefore, the gauche correction for 18 should be -1.3

times the gauche correction for 15. This yields an estimated value of -0.41. Using this gauche correction, along with the previously estimated group value for [C-H_2FC], allows one to estimate the $\Delta H_f^\circ(CH_2FCH_2CH_3)$ as -68.2 kcal/mole (-68.3 kcal/mole literature value[50]).

Assuming two such gauche effects in 18, and using the ΔH for 17 $\rightleftharpoons$ 18, one can estimate the group value for [C-F_2CC_D] (equation 17).

gauche corr. (18) = -0.82 16

[C-F_2CC_D] = -103.9 17

Previously, it was shown that a fluoroalkyl group value could be converted to a fluoroallylic group value by estimating the destabilization per fluorine, which was estimated to be 0.5 per fluorine. Assuming that the effect is the same whether the fluorines are on a terminal carbon or on an internal carbon, allows one to estimate [C-F_2C_2] (equation 18).

[C-F_2C_2] = -104.9 18

The group values estimated in this work are summarized below.

	Equation
$[C\text{-}H_2FC] = -52.7$	1
$(C\text{-}HF_2C] = -108.6$	2
$[C\text{-}F_3C] = -167.8$	3
$[C\text{-}F_2C_2] = -104.9$	18
$[C\text{-}H_2FC_D] = -52.2$	12
$[C\text{-}HF_2C_D] = -107.6$	10
$[C\text{-}F_3C_D] = -166.0$	11
$[C\text{-}F_2CC_D] = -103.9$	17
$[C_D\text{-}HF] = -38.4$	13
$[C_D\text{-}F_2] = -88.0$	15
cis corr. (CHF_2 cis to CH_2) = 1.37	6
cis corr. (CF_3 cis to CH_2) = 1.63	7
cis corr. (F cis to CH_3) = -0.64	14
gauche corr. (22) = 0.89	8
gauche corr. (25) = 1.05	9
gauche corr. (18) = -0.82	16

There are but a handful of experimentally determined ΔH_f°'s with which to test the efficacy of these group values. In the table below, it can be seen that the experimentally determined ΔH_f°'s and the ΔH_f°'s estimated using group values,

determined in this work, are in much better agreement than the ΔH_f°'s estimated using S. W. Benson's fluorine containing group values. The estimated ΔH_f° for trifluoromethylbenzene

	ΔH_f° (kcal/mole)[50]	ΔH_f° (kcal/mole)	ΔH_f° (kcal/mole)
	experimental	estimated[a]	estimated[b]
$FCH_2CH_2CH_3$	-68.3 ± 0.5	-68.2	-66.6
$CH_2{=}CHF$	-33.2 ± 0.4	-32.1	-31.3
$CH_2{=}CF_2$	-80.1 ± 0.8	-81.7	-71.2
$CF_3CH{=}CH_2$	-146.8 ± 1.6	-152.8	
$CF_3C_6H_5$	-143.2 ± 0.2	-144.0	
$CHF{=}CF_2$	-117 ± 2	-126.4	
$CF_2{=}CF_2$	-157.9 ± 0.4	-176.0	

[a] Estimated using group values derived in this work.

[b] Estimated using S. W. Benson's fluorine containing group values.[49]

is in good agreement with the experimentally determined value. However, for 3,3,3-trifluoropropene, there is a 6 kcal/mole discrepancy between the experimental and estimated ΔH_f°. This discrepancy may well be due to the experimental ΔH_f° for 3,3,3-trifluoropropene. However, it cannot be ruled out that the experimental ΔH_f° for both trifluorobenzene and trifluoroethane are in error and the error is of the same size sign and magnitude.

Trifluoroethene and tetrafluoroethene demonstrate the fallacy of using these group values in molecules where fluorine is contained in adjacent groups. There is a destabilizing effect across the double bond that raises the experimentally derived heats of formation. Alfassi et al. also discussed this problem, but in relation to trichloroethene and tetrachloroethene.[32]

A disproportion reaction is a hypothetical reaction in which a reorganization of structure occurs, but with no net change in the number or types of bonds. In the mono-substituted compounds there would exist no substituent-substituent interactions. Therefore, the mono-substituted compounds are taken as the molecular energy baseline to which the geminal effects are to be compared.[52] A positive

$$CH_3CHR_2 + CH_3CH_2 \longrightarrow CH_3CH_2R + CH_3CH_2R$$

enthalpy represents a stabilizing geminal effect and a negative enthalpy represents a destabilizing geminal effect.

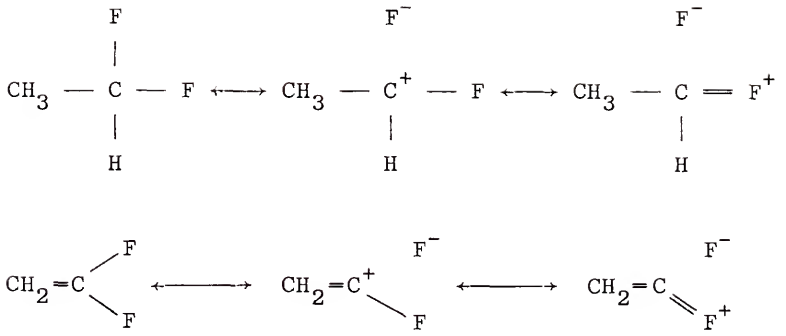
The geminal effect is slightly stabilizing for methyl (equation 19) and destabilizing for chlorine (equation 29). The geminal effect is very stabilizing for methoxy (equation 21) and alkyl fluorine (equation 23). A manifestation of this effect may also be seen in the fluorinated methanes, where the C-F bond strength increases upon adding the second fluorine to fluoromethane.[5,8,9]

	ΔΔH (kcal/mole)	
$CH_3CH(CH_3)_2 + CH_3CH_3 \rightarrow 2\ CH_3CH_2CH_3$	2.3	19
$CH_3CHCl_2 + CH_3CH_3 \rightarrow 2\ CH_3CH_2Cl$	-3.0	20
$CH_3CH(OCH_3)_2 + CH_3CH_3 \rightarrow 2\ CH_3CH_2OCH_3$	9.8	21
$CH_3CHF_2 + CH_3CH_3 \rightarrow 2\ CH_3CH_2F$	13.4	22
$CH_2{=}CHCHF_2 + CH_2{=}CHCH_3 \rightarrow 2\ CH_2{=}CHCH_2F$	13.2	23

Disproportional reactions can also be used to evaluate the geminal stabilization for vinylic substituents.[53] The geminal methyl groups exhibit very little geminal stabilization (equation 24). The geminal fluorine and chlorine substituents are about equally stabilizing. However, 8.4 kcal/mole of geminal stabilization is lost when the geminal

	ΔΔH (kcal/mole)	
$CH_2{=}C(CH_3)_2 + CH_2{=}CH_2 \rightarrow 2\ CH_2{=}CHCH_3$	1.2	24
$CH_2{=}CCl_2 + CH_2{=}CH_2 \rightarrow 2\ CH_2{=}CHCl$	4.8	25
$CH_2{=}CF_2 + CH_2{=}CH_2 \rightarrow 2\ CH_2{=}CHF$	5.0	26

fluorines are changed from alkyl to vinylic. This loss of geminal stabilization has been rationalized by invoking double-bond no-bond resonance structures. The two resonance forms for 1,1-difluoroethene would not be expected to contribute much to the overall stability of the compound.[52] The reason why the alkyl geminal chlorines exhibit no geminal



stabilization and the allylic geminal chlorines exhibit some geminal stabilization has not been discussed in the literature and is not apparent to the author.

Isodesmic equations such as 27 through 29 have been used to assess the effect of a substituent upon a double bond.[54] In equation 27, there is no net gain or loss of atoms. However, it does compare the strength of a sp^2-sp^2 sigma bond and a p-p pi bond on the left hand side to two sp^3-sp^3 sigma bonds on the right. Therefore, this type of hypothetical reaction gives an estimate of the double

	$\Delta\Delta H$ (kcal/mole)	
$CH_2{=}CH_2 + 2\ CH_3CH_3 \rightarrow 2\ CH_3CH_2CH_3$	-22.3	27
$CH_3CH{=}CH_2 + 2\ CH_3CH_3 \rightarrow CH_3CH_2CH_3 +$ $CH_3CH(CH_3)CH_3$	-21.4	28
$CH_3CH{=}CHCH_3 + 2\ CH_3CH_3 \rightarrow 2\ CH_3CH(CH_3)CH_3$	-21.2	29

bond strength. Hydrogen is taken as providing zero stabilization. Therefore, if the isodesmic equation for a substituted ethene is more exothermic than -22.3 kcal/mole, then the substituent is said to be destabilizing relative to a hydrogen. A $\Delta\Delta H$ greater than -22.3 kcal/mole implies stabilization. One or two methyl groups are slightly stabilizing (equations 28 and 29). However, chlorine and bromine are clearly destabilizing relative to hydrogen (equations 30 and 31).

	$\Delta\Delta H$ (kcal/mole)	
$CH_2{=}CHCl + 2\ CH_3CH_3 \rightarrow CH_3CH_2CH_3 +$ $CH_3CHClCH_3$	-28.4	30
$CH_2{=}CHBr + 2\ CH_3CH_3 \rightarrow CH_3CH_2CH_3 +$ $CH_3CHBrCH_3$	-27.3	31

It is important to bear in mind what effect the double bond stability has on an equilibrium where the substituent, R, is either allylic or vinylic (equation 32). Methyl groups

$$CH_2{=}CHCH_2R \rightleftharpoons CH_3CH{=}CHR \qquad 32$$

$$CH_2{=}CHCH_2CH_3 \rightleftharpoons CH_3CH{=}CHCH_3 \quad \Delta H = 3.1 \text{ kcal/mole} \qquad 33$$

are slightly stabilizing towards the double bond and they prefer to be vinylic (equation 33).[37] Since chlorine

and bromine destabilize the double bond, one would expect allylic chlorine or bromine to be thermodynamically more stable than the vinylic chlorine or bromine. However, experimental evidence clearly shows that they prefer to be vinylic (equations 34 and 35).[26] Therefore, the stability of the double bond is only one factor that is

$$CH_2{=}CHCH_2Cl \rightleftharpoons CH_3CH{=}CHCl \qquad \Delta H = -2.6 \text{ kcal/mole} \qquad 34$$

$$CH_2{=}CHCH_2Br \rightleftharpoons CH_3CH{=}CHBr \qquad \Delta H = -0.7 \text{ kcal/mole} \qquad 35$$

involved in this type of equilibrium. Clearly there are other factors that are more important than the double bond stability.

One fluorine has very little effect upon the double bond (equation 36). In the isomerization of fluoropropene, the fluorine ends up vinylic, as expected (equation 37).

$$CH_2{=}CHF + 2\ CH_3CH_3 \rightarrow CH_3CH_2CH_3 + CH_3CHFCH_3 \qquad \Delta\Delta H = -22.8 \text{ kcal/mole} \qquad 36$$

$$CH_2FCH{=}CH_2 \rightleftharpoons CHF{=}CHCH_3 \qquad \Delta H = -2.68 \text{ kcal/mole} \qquad 37$$

$$\underline{26} \qquad\qquad \underline{27t}$$

Geminal fluorines appear to have a destabilizing effect upon the double bond (equation 38). By comparison to chloropropene (equation 34) and bromopropene (equation 35), 1,1-difluoropropene should be the thermodynamically favored

compound. However, this was not observed (equation 39). The major factor in the equilibrium is the strong geminal

$$CH_2{=}CF_2 + CH_3CH_3 \rightarrow CH_3CH_2CH_3 + CH_3CF_2CH_3 \qquad \Delta\Delta H = -28.4 \text{ kcal/mole} \qquad 38$$

$$CF_2HCH{=}CH_2 \rightleftharpoons CF_2{=}CHCH_3 \qquad \Delta H = +2.5 \text{ kcal/mole} \qquad 39$$

$$\underline{28} \qquad\qquad \underline{29}$$

fluorine stabilization present in 3,3-difluoropropene. This effect predominates, causing the equilibrium to be shifted towards the allylic geminal fluorines.

From the kinetics of converting 17 to 18, an E_a of 33.0 kcal/mole was found. This value is 2.5 kcal/mole lower than the E_a for the rearrangement of 1,1-dideutero-1,5-hexadiene.[36] This lowering may be attributed to an increase in the geminal fluorine stabilization in the transition state, where the hybridization of the difluoromethylene group is changed from sp^2 to sp^3.

CHAPTER IV
EXPERIMENTAL

^{19}F NMR spectra were determined on a XL-100 instrument at 94.1 MHz. Chemical shifts are reported in ppm from internal $CFCl_3$ with $CDCl_3$ as the solvent.

All ^{1}H NMR spectra were determined at 60 MHz. 18 was determined on a JEOL JNM-PMX. 17 and 19 were determined on a Varian EM360L. All other spectra were determined on a Varian A-60A. Chemical shifts are reported in ppm downfield from internal TMS with $CDCl_3$ as the solvent.

Infrared spectra were determined on a Perkin-Elmer 283B spectrophotometer. Absorption bands are reported in cm^{-1}. The spectra were determined from the neat liquid between KCl plates, unless otherwise stated.

Mass spectra and exact masses were determined on an AEI-MS 30 spectrometer at 70 eV.

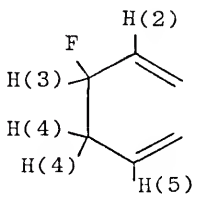
Preparative glpc separations were accomplished on a Varian Aerograph 90-P using helium as the carrier gas and fitted with either column 1 (10' x 1/4" 10% ODPN on Chromosorb P 60/80) or column 2 (10' x 1/4" 10% DNP on Chromosorb P 60/80). Product ratios and kinetic data were determined on a Hewlett-Packard 5710A fitted with a flame ionization detector, gas injection system and a Hewlett-

Packard 3380S integrator. Either column 3 (7' x 1/8" 10% ODPN on Chromosorb P 60/80) or column 4 (10' x 1/8" 10% DNP on Chromosorb P 60/80) was used.

Thermolyses were carried out in a well-conditioned 100 ml pyrex vessel suspended in a thermostated molten salt bath.

3-Fluoro-1,5-hexadiene, 16

A three-necked flask was equipped with a rubber septum, drying tube, alcohol thermometer, and 2 g DAST[38] in a 5 ml dry methylene chloride. The solution was cooled to -78°, then 1.2 g of 1,5-hexadiene-3-ol(Aldrich) was slowly added. After the addition was complete, the reaction was allowed to warm to room temperature. It was washed with Na_2CO_3/ H_2O and dried with $MgSO_4$. 16 was isolated by preparative glpc on column 1 and 0.32 g of 16, 96% glpc pure, was collected for a 25% yield.



16

^{19}F NMR (figure 1); ϕ 177.6 (dtd, $J_{FH(3)}$ = 48 Hz, $J_{FH(4)}$ = 21 Hz, $J_{FH(2)}$ = 14.5 Hz).

^{1}H NMR (figure 2); δ 4.9-6.4 (6H, m), 4.95 (1H, dq, $J_{H(3)F}$ = 48 Hz, $J_{H(3)H(4)}$ = 6 Hz, $J_{H(3)H(2)}$ = 6 Hz), 2.45 (2H, dt, $J_{H(4)F}$ = 21 Hz, $J_{H(4)H(3)}$ = 6 Hz, $J_{H(4)H(5)}$ = 6 Hz).

IR (gas) (figure 3); 3100 (m), 3005 (m), 2940 (m), 1650 (w), 1430 (w), 1340 (w), 995 (s), 930 (s), 735 (m) cm^{-1}.

Mass spectrum gave M^+ 100.0679 ± 0.00094 (9.4 ppm), calculated for C_6H_9F: 100.0688, deviation = 0.00089 (8.9 ppm); m/e (relative intensity): 100 (1.0, 99 (3), 85 (22), 80 (21), 79 (31), 77 (14), 72 (20), 67 (13), 59 (100), 41 (44).

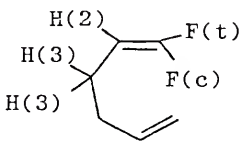
Thermolysis of 16

Five millimeters of 16 was expanded into the thermolysis bulb which was maintained at 160°. The progress of the reaction was followed by glpc on column 3. All of 16 was consumed and two major products were produced, along with many minor products. The two major products were isolated and identified by their ^{1}H NMR as 1,3,5-hexatriene and 1,3-cyclohexadiene.

1,1-Difluoro-1,5-hexadiene, 17

17 was prepared by the method of Naae and Burton.[40] A 100 ml three-necked flask was equipped with a distillation take-off, constant pressure addition funnel, and a

thermometer. Previously, the reagents and apparatus were dried. Then 4.2 g of pentenal,[39] 10.5 g of dibromodifluoromethane (PCR), and 30 ml of triglyme were placed in the flask. In the addition funnel was placed 16.3 g HMPT (Aldrich) in 20 ml triglyme. The reaction was cooled with ice and the HMPT was added, keeping the temperature below 15°. After addition was complete, the reaction was allowed to warm to room temperature and stirred for 4 h. The product was removed by flash vacuum distillation. The product was purified by preparative glpc on column 1 and 0.56 g 17 was collected for a 9.5% yield.



17

^{19}F NMR (figure 4); ϕ 82.8 (1F, d, $J_{F(t)F(c)}$ = 40 Hz), 86.2 (1F, dd, $J_{F(c)F(t)}$ = 40 Hz, $J_{F(c)H(2)}$ = 21 Hz).

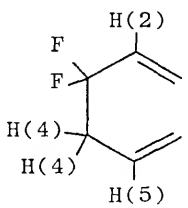
^{1}H NMR (figure 5); δ 5.3-6.2 (1H, m), 4.8-5.3 (2H, m), 4.1 (1H, dtd, $J_{H(2)F(c)}$ = 21 Hz, $J_{H(2)H(3)}$ = 8 Hz, $J_{H(2)F(t)}$ = 4 Hz), 2.15 (4H, broad s).

IR (gas) (figure 6); 3000 (w), 2940 (m), 2870 (w), 1750 (s), 1645 (w), 1450 (w), 1350 (w), 1315 (s), 1240 (s), 1190 (s), 920 (s), 800 (w), cm^{-1}.

Mass spectrum gave M^+ 118.0593 ± 0.00057 (4.8 ppm), calculated for $C_6H_8F_2$: 118.0594, deviation = 0.000077 (0.65 ppm); m/e (relative intensity): 118 (1.3), 103 (3), 98 (5), 77 (100), 67 (5), 54 (16), 51 (20), 41 (24), 39 (21).

3,3-Difluoro-1,5-hexadiene, 18

Twenty millimeters of 17 was expanded into a well-conditioned pyrolysis bulk at 245°. After 30 min the products were condensed into a storage bulb. Several runs were combined and separated by preparative glpc on column 1. No detectable amount of 17 remained.



18

^{19}F NMR (figure 7); ϕ 97.9 (td, $J_{FH(4)}$ = 16.2 Hz, $J_{FH(2)}$ = 9.4 Hz).

^{1}NMR (figure 8); δ 5.0-6.5 (6H, m), 2.7 (2H, td, $J_{H(4)F}$ = 16.2 Hz, $J_{H(4)H(5)}$ = 6 Hz).

IR (gas) (figure 9); 3100 (m), 3000 (w), 2940 (w), 1650 (w), 1425 (s), 1300 (m), 1160 (s), 1100 (s), 1040 (m), 990 (s), 950 (m), 925 (m), 890 (w) cm^{-1}.

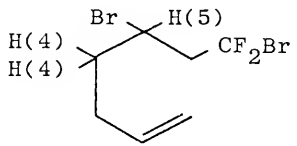
Mass spectrum gave M^+ 118.0577 ± 0.001 (8.7 ppm), calculated for $C_6H_8F_2$: 118.0594, deviation = 0.0017 (14.6 ppm); m/e (relative intensity): 118 (1.5), 103 (3), 98 (8), 90 (4), 77 (100), 67 (3), 54 (16), 51 (17), 41 (22), 39 (15).

Thermolysis of 17 and 18

Five millimeters of 17 was pyrolyzed at six temperatures between 194.3° and 214.6°. The reaction was followed by glpc using column 3. The rate data and rate constants are listed in table 1, along with the resulting equilibrium constants. In table 2, the results from the Arrhenius plot of the rate constants are tabulated. The ΔG value obtained from the equilibrium constant at 194.3° was omitted and the remaining five ΔG's were averaged to yield a ΔG_{avg} of 5.1 ± 0.3 kcal/mole at an average temperature of 206.6°. The mass balance for the reaction was 99.7%, using pentane as an internal standard. The same equilibrium constant, within experimental error, was obtained starting from either 17 or 18.

5,7-Dibromo-7,7-difluoro-1-heptene, 19

In a dry 250 ml autoclave was placed 3.6 g of benzoyl peroxide, 30 g of 1,5-hexadiene, and 115 g dibromodifluoromethane. It was heated with rocking at 100° for 6.5 h. Distillation yielded unreacted starting material and 29.3 g of 19, bp 68-70°, at 4 mm, 27% yield.



19

^{19}F NMR (figure 10); ϕ 43.3 (t, $J_{FH(6)}$ = 13.6 Hz).

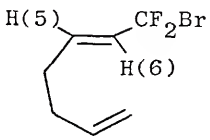
^{1}H NMR (figure 11); δ 5.3-6.2 (1H, m), 4.8-5.3 (2H, m), 4.2 (1H, p, $J_{H(5)H(4)}$ = 6 Hz, $J_{H(5)H(4)}$ = 6 Hz), 2.7-3.5 (2H, m), 1.7-2.7 (4H, m).

IR (figure 12); 3100 (w), 2995 (w), 2930 (m), 2860 (w), 1650 (m), 1450 (w), 1435 (w), 1200 (s), 1100 (s), 1000 (s), 920 (s), 760 (w), 635 (m), 550 (m) cm^{-1}.

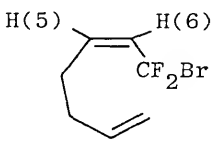
Mass spectrum gave M^+ 289.9122 ± 0.00418 (14.4 ppm), calculated for $C_7H_{10}F_2Br_2$: 289.9118, deviation = 0.00042 (1.5 ppm); m/e (relative intensity): 294 (0.1), 292 (0.4), 290 (0.1), 252 (0.4), 251 (0.1), 250 (0.8), 131 (10), 111 (11), 91 (11), 81 (10), 67 (25), 55 (11), 28 (100).

7-Bromo-7,7-difluoro-1,5-heptadiene, 20t and 20c

A three-necked 250 ml flask was equipped with an addition funnel and a distillation take-off with a 6-inch vigreux column. In the flask was placed 10 g of potassium hydroxide and 16.4 g 19 was placed in the addition funnel. The pressure was reduced to 30 mm and the flask was heated to 120°. 19 was slowly added and a mixture of 19 and 20 was distilled out. Redistillation of the distillate yielded 6.8 g 20, bp_{15} 55°, and 4.3 g 19. Yield based on amount of 19 used was 77.3%, 5% 20c and 95% 20t.



20t



20c

^{19}F NMR (figure 13); 20c ϕ 39.3 (2F, 2m, $J_{FH(6)}$ = 13.8 Hz), 20t ϕ 44.6 (2F, dd, $J_{FH(6)}$ = 9.0 Hz, $J_{FH(5)}$ = 1.4 Hz).

^{1}H NMR (figure 14); δ 5.3-6.7 (3H, m) 4.8-5.3 (2H, m), 2.1-2.5 (4H, broad s).

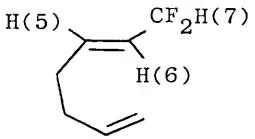
IR (figure 15); 3095 (w), 2995 (w), 2940 (w), 2860 (w), 1740 (m), 1730 (m), 1675 (m), 1650 (m), 1450 (w), 1350

(w), 1300 (w), 1230 (s), 1190 (w), 1090 (m), 920 (s), 735 (m) cm^{-1}.

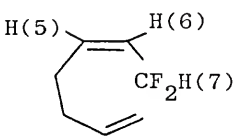
Mass spectrum gave insufficient parent ion for exact mass; m/e (relative intensity): 212 (0.2), 210 (0.2), 171 (1), 169 (1), 131 (38), 111 (13), 90 (38), 41 (53), 28 (100).

7,7-Difluoro-1,5-heptadiene 21c and 21t

In a 25 ml flask was stirred 3.5 g of tri-n-butyltin hydride[41] and 2 g of 20 for 4 h at room temperature. The mixture was flash vacuum distilled and preparative glpc on column 2 yielded 0.5 g 21, for a 42% yield. 21 was 97.7% glpc pure on column 4, bp 120-122°, and composed of 95% 21t and 5% 21c.



21t



21c

^{19}F NMR (figure 16); 21t ϕ 110.3 (2F, 2m, $J_{FH(7)}$ = 59.5 Hz), 21c ϕ 111.4 (2F, ddt, $J_{FH(7)}$ = 56.0 Hz, $J_{FH(6)}$ = 8.2 Hz).

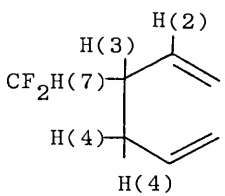
^{1}H NMR (figure 17); δ 5.9 (1H, td, $J_{H(7)F}$ = 59.5 Hz, $J_{H(7)H(6)}$ = 5 Hz), 5.2-6.4 (3H, m), 4.8-5.2 (2H, m), 2.0-2.4 (4H, broad s).

IR (gas) (figure 18); 3095 (w), 2995 (w), 2940 (w), 2860 (w), 1680 (m), 1645 (m), 1395 (m), 1145 (m), 1130 (m), 1020 (s), 970 (m), 915 (m) cm^{-1}.

Mass spectrum gave insufficient parent ion for exact mass: m/e (relative intensity): 132 (0.3), 131 (0.2), 117 (1), 104 (5), 97 (3), 91 (4), 81 (69), 72 (14), 59 (6), 41 (100).

3-Difluoromethyl-1,5-hexadiene, 22

21 was pyrolyzed at 350° for 5 minutes, which yielded an equilibrium mixture of 21 and 22. Several runs were combined and separated by preparative glpc on column 2.



22

^{19}F NMR (figure 19); ϕ 123.5 (dd, $J_{FH(7)}$ = 56.7 Hz, $J_{FH(3)}$ = 15.1 Hz).

^{1}H NMR (figure 20); δ 5.74 (1H, td, $J_{H(7)F}$ = 56.7 Hz, $J_{H(7)H(3)}$ = 3.5 Hz), 4.7-6.1 (6H, m), 2.0-3.0 (3H, m).

IR (gas) (figure 21); 3095 (w), 2998 (w), 2940 (w), 1645 (w), 1450 (w), 1425 (w), 1380 (m), 1140 (m), 1090 (m), 1050 (m), 720 (w) cm^{-1}.

Mass spectrum gave insufficient parent ion for exact mass: m/e (relative intensity): 131 (0.2), 104 (3), 91 (3), 81 (80), 77 (6), 72 (16), 53 (11), 51 (12), 41 (100).

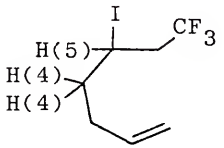
Thermolysis of 22, 21c, and 21t

22 was pyrolyzed in a well-conditioned pyrex vessel from 309.9° to 409.0°. 21c and 21t were pyrolyzed at 409.0°. The resulting equilibrium mixtures were analyzed on column 4. The equilibrium values are listed in table 3. Table 4 contains the results from the van't Hoff plots, along with the correlation coefficient for each plot. The mass balance was 97.6%, using pentane as the internal standard.

5-Iodo-7,7,7-trifluoro-1-heptene, 23

In a 200 ml tube was sealed 14.8 g of trifluoromethyl iodide and 6.5 g of 1,5-hexadiene. It was irradiated in a Rayonet Photochemical Reactor. After 24 h, the tube was cooled in liquid nitrogen and opened. Eleven grams of trifluoromethyl iodide was recovered and the remaining mixture was

vacuum distilled to yield 23, bp_4 48°. Based on the amount of trifluoromethyl iodide used, the yield was 60%.



23

^{19}F NMR (figure 22); ϕ 64.4 (t, $J_{FH(6)}$ = 10.4 Hz).

^{1}H NMR (figure 23); δ 5.5-6.2 (1H, m), 4.9-5.4 (2H, m), 4.2 (1H, p, $J_{H(5)H(4)}$ = 7 Hz, $J_{H(5)H(6)}$ = 7 Hz), 2.5-3.3 (2H, m), 1.6-2.5 (4H, m).

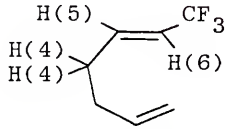
IR (figure 24); 3090 (w), 2990 (w), 2940 (m), 2960 (w), 1650 (m), 1435 (m), 1360 (m), 1260 (s), 1150 (s), 995 (w), 920 (m), 580 (w) cm^{-1}.

Mass spectrum gave M^+ 277.9788 ± 0.00152 (5.5 ppm), calculated for $C_7H_{10}F_3I$: 277.9779, deviation = 0.0007 (2.5 ppm); m/e (relative intensity); 278 (3.8), 237 (1), 151 (59), 131 (29), 123 (11), 41 (100).

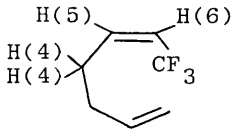
7,7,7-Trifluoro-1,5-heptadiene 24t and 24c

In a 100 ml flask, equipped with a 6" vigreux distillation apparatus, was placed 2.95 g 23 and 1.5 g of potassium hydroxide. These were heated at 120° for

20 minutes. The products were flash vacuum distilled from the solids. Preparative glpc on column 2 yielded 0.58 g 24, bp 96-97°, and 0.6 g 23. 24 was 14% 24c and 86% 24t. Overall purity was 99.5% and yield based on the amount of 23 used was 47%.



24t



24c

^{19}F NMR (figure 24); 24c ϕ 58.9 (dt, $J_{FH(6)}$ = 8.3 Hz, $J_{FH(4)}$ = 2.2 Hz), 24t ϕ 64.6 (2m, $J_{FH(6)}$ = 6.2 Hz).

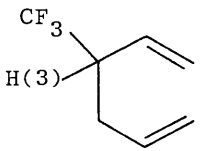
^{1}H NMR (figure 26); δ 5.3-6.8 (3H, m), 4.8-5.3 (2H, m), 2.1-2.5 (4H, broad s).

IR (gas) (figure 27); 3100 (w), 3000 (w), 2950 (m), 2860 (w), 1690 (m), 1650 (w), 1450 (w), 1425 (w), 1330 (m), 1275 (s), 1200 (w), 1125 (s), 980 (m), 920 (s) cm^{-1}.

Mass spectrum gave M^+ 150.0647 ± 0.00168 (11.2 ppm), calculated for $C_7H_9F_3$: 150.0656, deviation = 0.00086 (5.8 ppm); m/e (relative intensity): 150 (0.5), 135 (7), 130 (4), 115 (5), 81 (27), 77 (8), 41 (98), 28 (100).

3-Trifluoromethyl-1,5-hexadiene, 25

25 was made from 24 by the procedure previously outlined for 22. 25 was 98.6% glpc pure on column 4.



25

^{19}F NMR (figure 28); ϕ 71.5 (d, $J_{FH(3)}$ = 8.7 Hz).

^{1}H NMR (figure 29); δ 4.8-6.1 (6H, m), 2.0-3.2 (3H, m).

IR (gas) (figure 30); 3100 (m), 3000 (w), 2995 (w), 1860 (w), 1650 (m), 1430 (w), 1360 (m), 1310 (m), 1260 (s), 1190 (s), 1125 (s), 990 (m), 925 (s), 720 (m) cm^{-1}.

Mass spectrum gave M^+ 150.0647 ± 0.0024 (14.9 ppm), calculated for $C_7H_9F_3$: 150.0656, deviation = 0.0009 (6.0 ppm); m/e (relative intensity): 150 (0.1), 135 (5), 122 (4), 115 (4), 90 (3), 81 (29), 41 (100).

Thermolysis of 24c, 24t, and 25

25 was pyrolyzed in a well-conditioned glass vessel from 321.3° to 408.0° and a mixture of 24c and 24t was pyrolyzed at 408.0°. The resulting equilibrium mixtures

were analyzed on column 4. The values are listed in table 5. Table 6 contains the results of the van't Hoff plots, along with the correlation coefficients. The mass balance was 96.4% using pentane as an internal standard.

3-Fluoropropene, 26

The procedure outlined by F. W. Hoffman[43] was used to synthesize 26. A three-necked 500 ml flask was equipped with an overhead stirrer, pressure equalized addition funnel, and distillation take-off leading to a dry ice cooled trap. In 200 ml dry ethylene glycol, 66 g of potassium fluoride was heated to 130°-150°. Seventy grams 3-bromopropene was added and 16.5 g of 26 was isolated, 47.5% yield, 99.9% glpc pure on column 2. 26 was used without further purification. The ^{19}F NMR, ^{1}H NMR, and IR spectra were identical to those reported in the literature.[44,45]

Mass spectrum gave M^+ 60.0390 ± 0.0025 (41 ppm), calculated for C_3H_5F: 60.0375, deviation = 0.0015 (25 ppm); m/e (relative intensity): 60 (56), 59 (100), 58 (3), 57 (12), 41 (10).

1-Fluoropropene, 27c and 27t

26 was equilibrated with a catalytic amount of iodine. The equilibrium mixture of 26 and 27 was transferred through a 2" column containing 5% tetraethanepentamine on Chromosorb 60/80 and condensed into a storage vessel.

Several runs were combined and 27 was isolated by preparative glpc on column 1 at -20°. 27 was 99.9% pure on column 2. The ^{1}H NMR and ^{19}F NMR spectra were identical to those reported in the literature.[46]

IR (gas) (figure 31); 3100 (w), 2970 (w), 1700 (s), 1680 (s), 1250 (m), 1230 (m), 1150 (s), 1130 (s), 1110 (m), 1010 (s), 910 (m), 745 (s) cm^{-1}.

Mass spectrum gave M^{+} 60.0383 ± 0.00097 (16 ppm), calculated for C_3H_5F: 60.0375, deviation = 0.00079 (13 ppm); m/e (relative intensity): 60 (61), 59 (100), 58 (5), 57 (17), 39 (17).

Thermolysis of 26, 27c and 27t

A glass storage bulb containing a few crystals of iodine (Mallinckrodt) was connected to the vacuum line (maintained at 110°) containing the pyrolysis vessel. After degassing the iodine, the storage vessel was heated and some iodine was expanded into the pyrolysis vessel, which was then closed off from the vacuum line. The iodine remaining in the vacuum line was recondensed into the storage bulb. The appropriate amount of 26 or 27 was then expanded into the pyrolysis vessel. Since the vacuum line contained two well-conditioned pyrolysis vessels, two runs could be run simultaneously. It was found that the rate of propene formation varied from run to run. Equilibrium mixtures were evaluated on column 3

and the resulting data are listed in table 7. The results of the van't Hoff plots are listed in table 8.

3,3-Difluoropropene, 28

A three-necked 50 ml flask was equipped with a magnetic stirrer, rubber septum, thermometer and outlet pipe connected to a dry ice cooled trap. To the flask, 4.2 g DAST[38] was added and cooled to 0°. Then 1.5 g propenal was slowly added and stirred for 3 h. The product, 0.7 g 28, was collected, 98.8% glpc pure on column 3, 34% yield. The ^{1}H NMR and ^{19}F NMR matched data published in the literature.[44]

IR (gas) (figure 32); 3110 (w), 2975 (m), 1900 (w), 1680 (w), 1450 (m), 1350 (m), 1155 (m), 1050-1130 (s), 950 (m), 740 (w) cm^{-1}.

Mass spectrum gave M^{+} 78.0269 ± 0.0018 (23 ppm), calculated for $C_3H_4F_2$: 78.0281, deviation = 0.0012 (15 ppm); m/e (relative intensity): 78 (51), 77 (100), 76 (2), 75 (5), 64 (12), 59 (14), 57 (6), 51 (14).

1,1-Difluoropropene, 29

29 was made by the method of S. J. Moss and K. R. Jennings.[47] A trap containing 0.84 g of trifluoropropane was connected to a stainless steel tube containing silica chips and heated to 700°. The other end of the tube was connected to a potassium hydroxide trap, liquid nitrogen cooled trap, and a vacuum source. The gas collected in

the trap was separated by preparative glpc on column 1. 0.05 g 29 was collected, 7.5% yield, and 99.5% glpc pure on column 3. The ^{1}H NMR, ^{19}F NMR, and IR spectra matched those published in the literature.[48]

Mass spectrum gave M^{+} 78.02869 ± 0.00217 (28 ppm); calculated for $C_3H_4F_2$: 78.0281, deviation = 0.00058 (7 ppm); m/e (relative intensity): 79 (67), 78 (100), 77 (12), 76 (17), 59 (27), 58 (4), 52 (52).

Thermolysis of 28 and 29

28 and 29 were pyrolyzed with a catalytic amount of iodine between 378.3° and 412.8°. The equilibria were analyzed on column 3 and the results are listed in table 9. The entropy and enthalpy values obtained from the van't Hoff plots are listed in table 10. The mass balance was 97%, measured by pressure.

APPENDIX 1
^{1}H NMR, ^{19}F NMR, AND IR OF RELEVANT COMPOUNDS

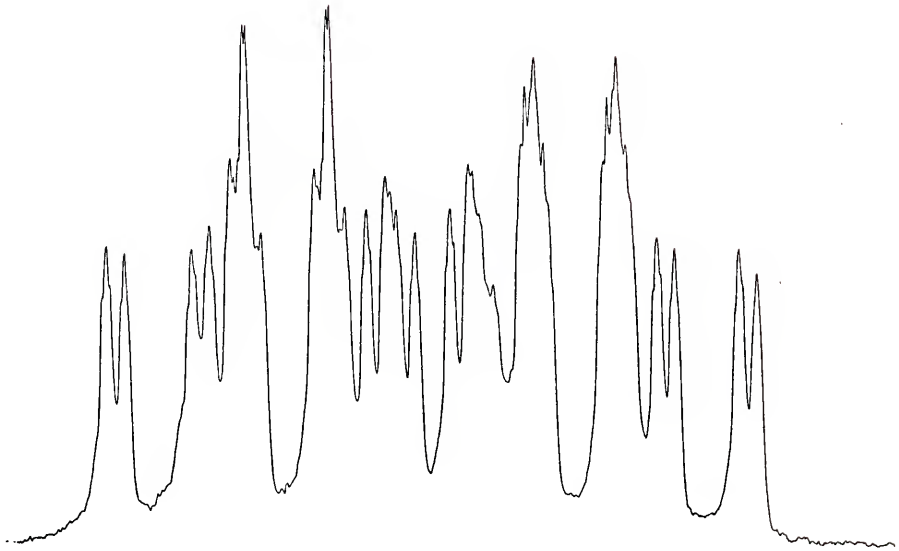


Figure 1. ^{19}F NMR of 3-Fluoro-1,5-hexadiene, 16, ϕ 177.6 ppm.

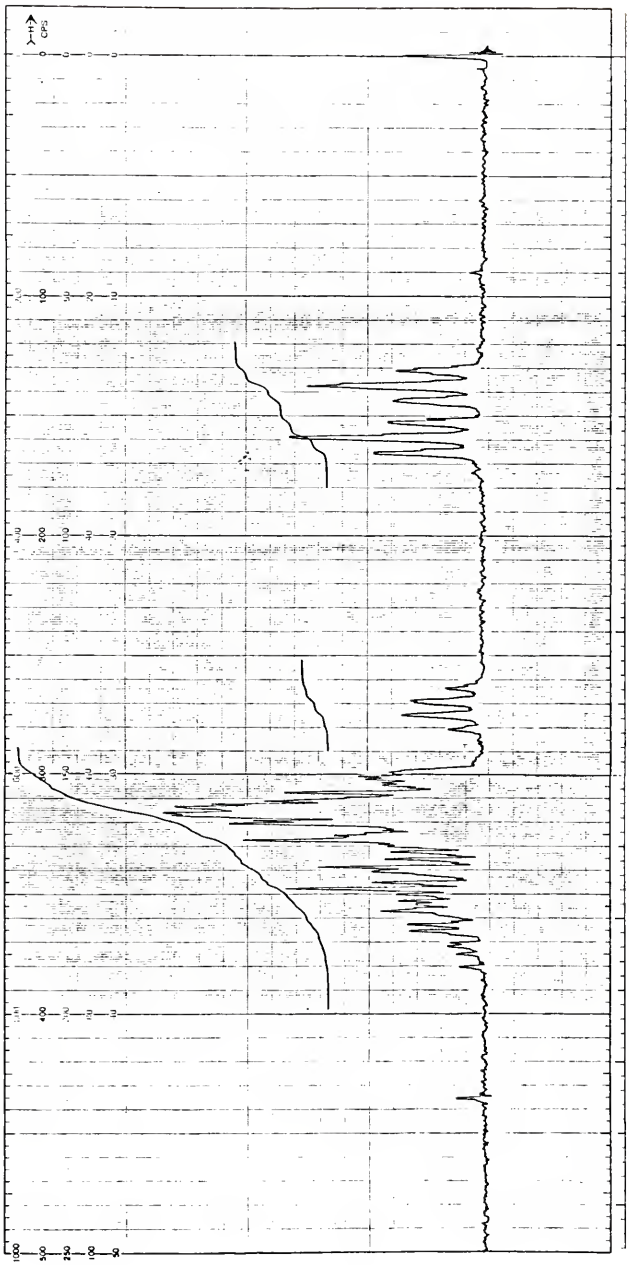


Figure 2. ^{1}H NMR of 3-Fluoro-1,5-hexadiene, 16.

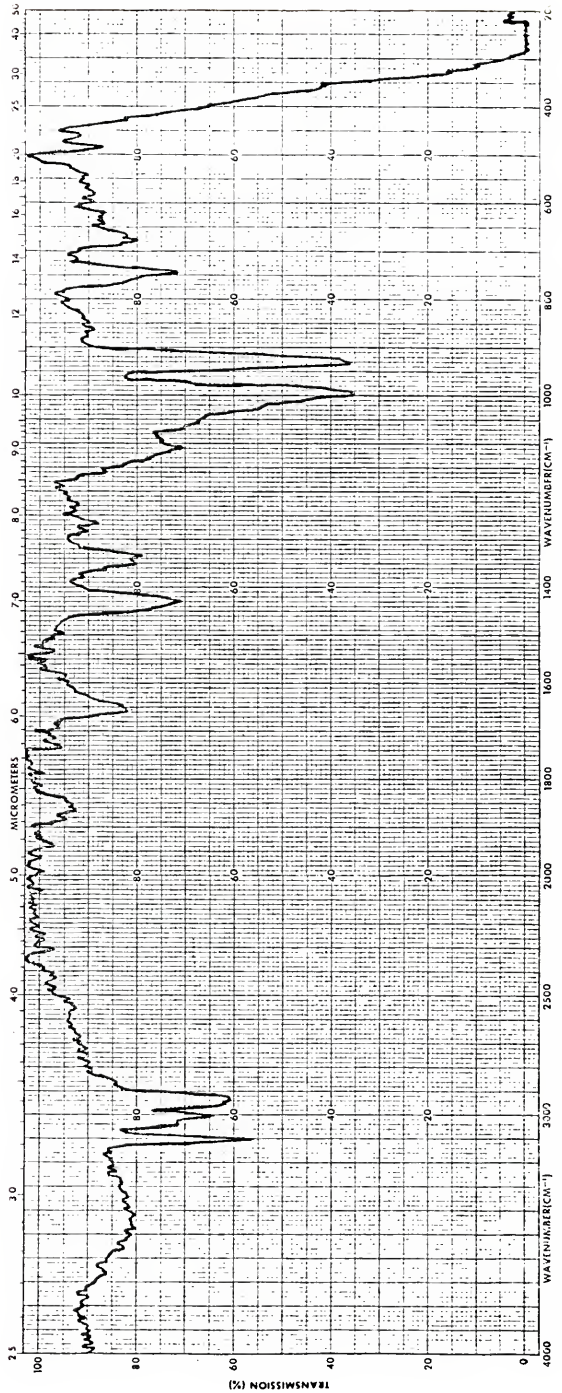


Figure 3. IR of 3-Fluoro-1,5-hexadiene, 16.

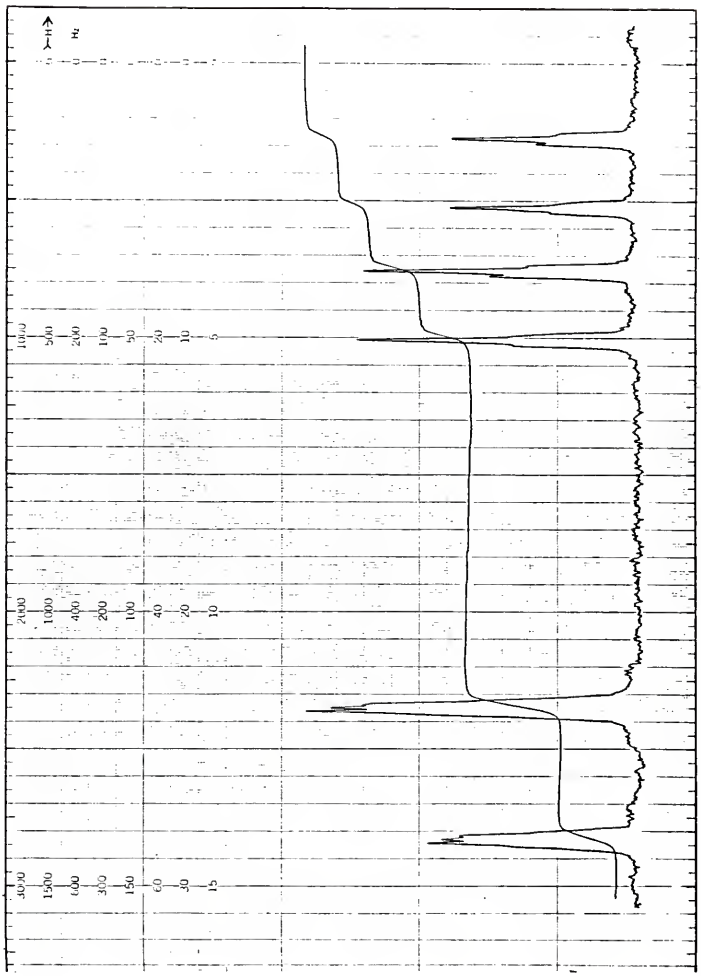


Figure 4. ^{19}F NMR of 1,1-Difluoro-1,5-hexadiene, 17 ϕ 84.5 ppm.

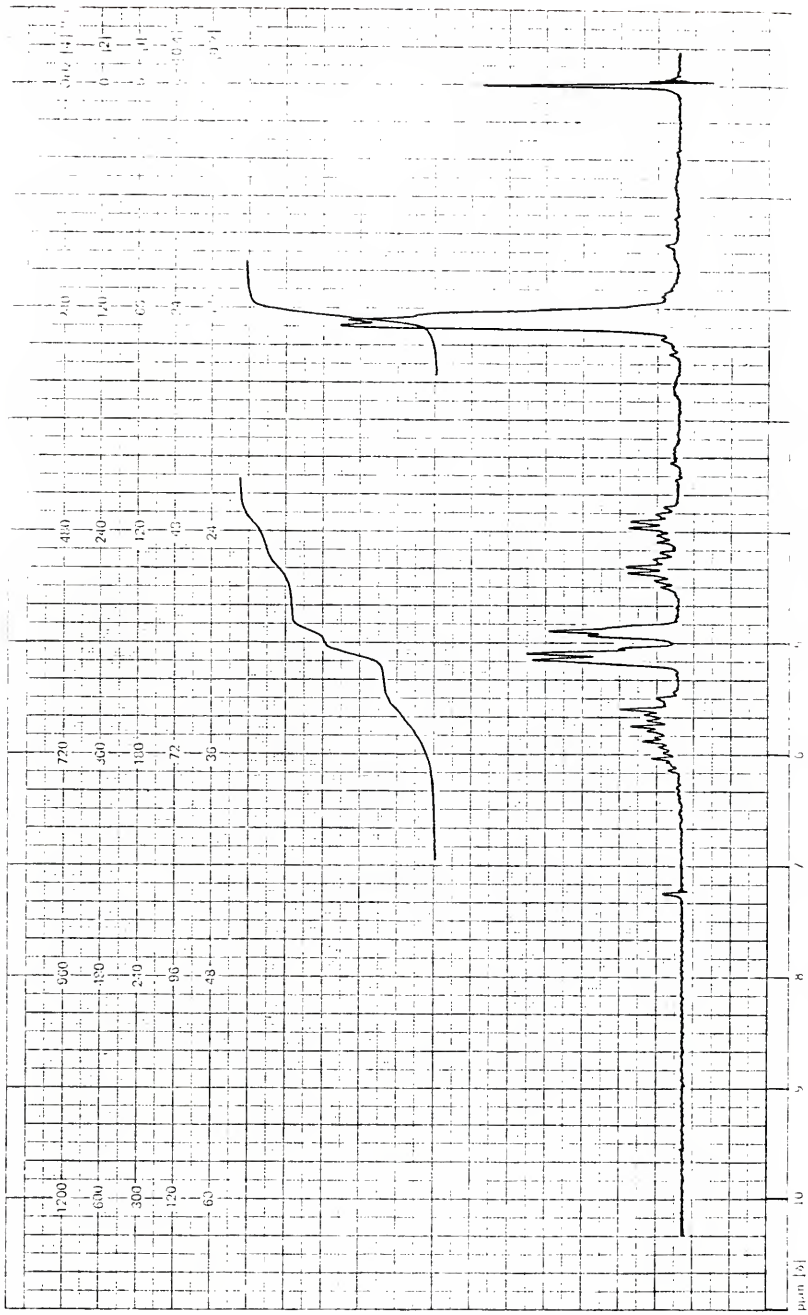


Figure 5. ^{1}H NMR of 1,1-Difluoro-1,5-hexadiene, 17.

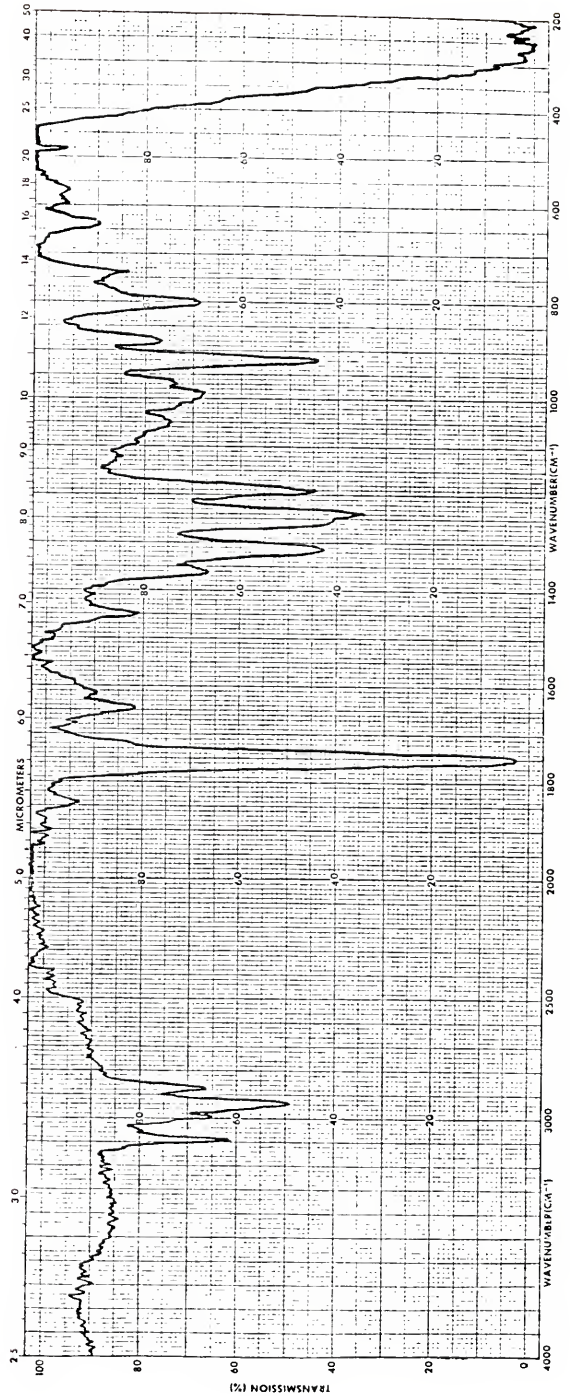


Figure 6. IR of 1,1-Difluoro-1,5-hexadiene, 17.

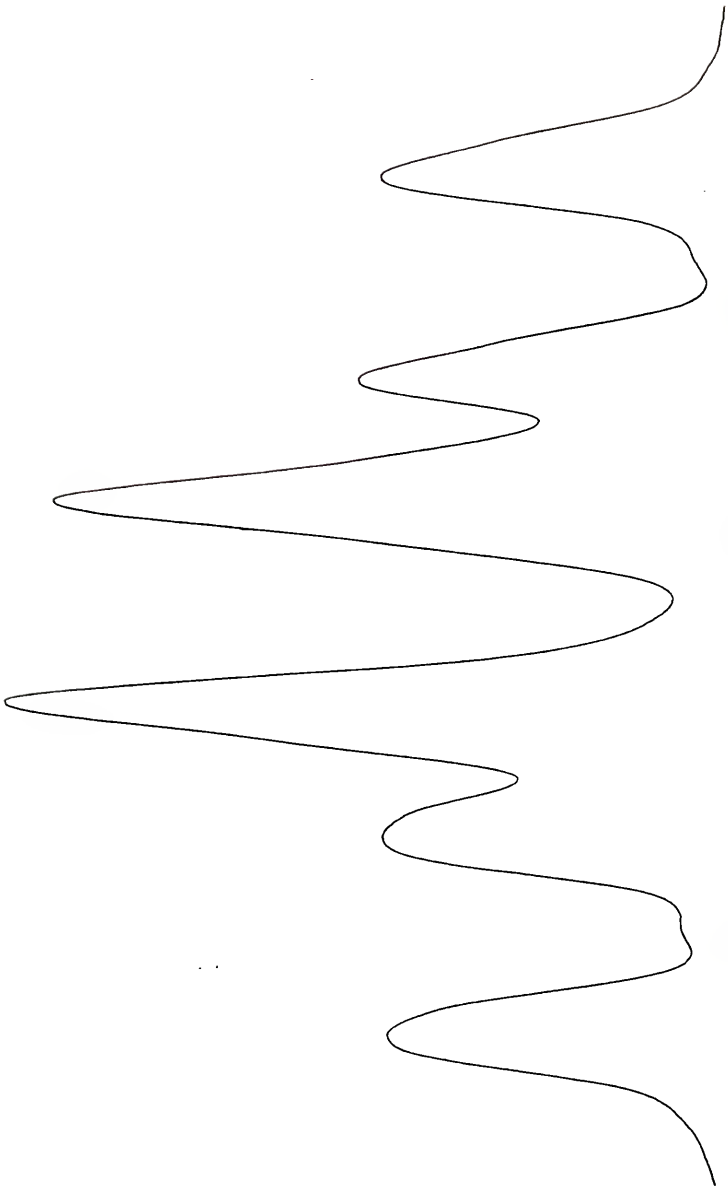


Figure 7. ^{19}F NMR of 3,3-Difluoro-1,5-hexadiene, 18, ϕ 97.9 ppm.

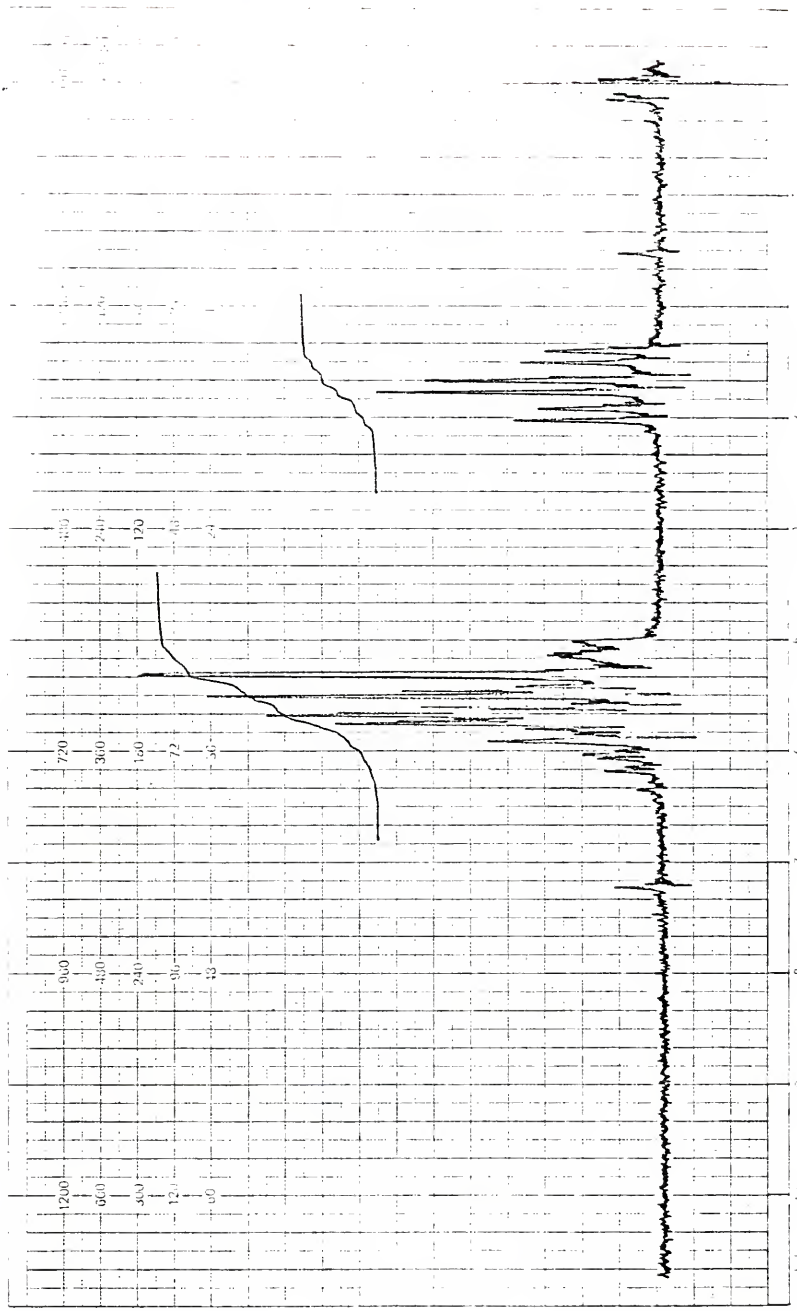


Figure 8. ^{1}H NMR of 3,3-Difluoro-1,5-hexadiene, 18.

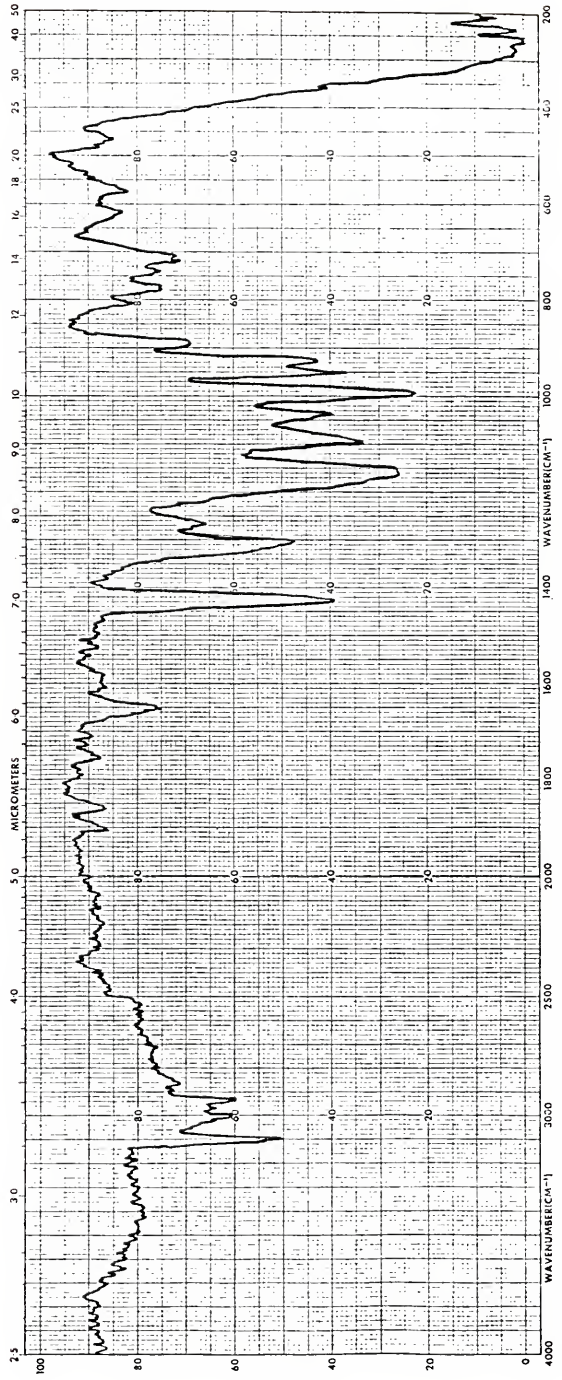


Figure 9. IR of 3,3-Difluoro-1,5-hexadiene, 18.

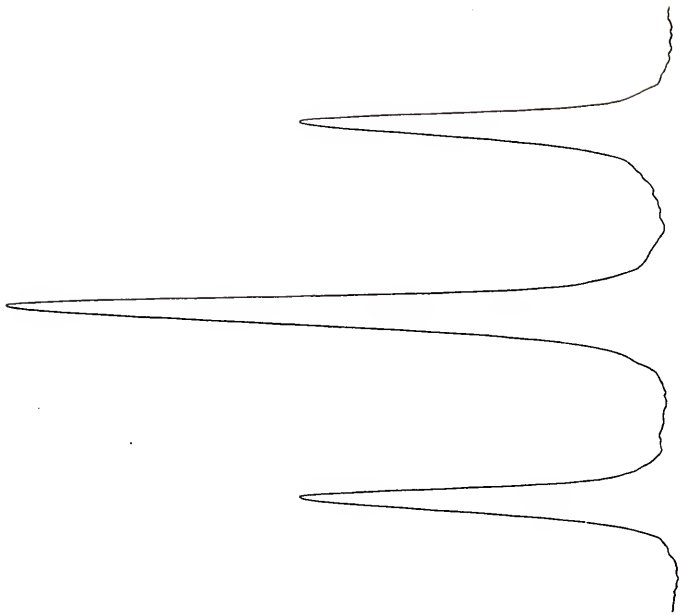


Figure 10. ^{19}F NMR of 5,7-Dibromo-7,7-difluoro-1-heptene, 19, ϕ 43.3 ppm.

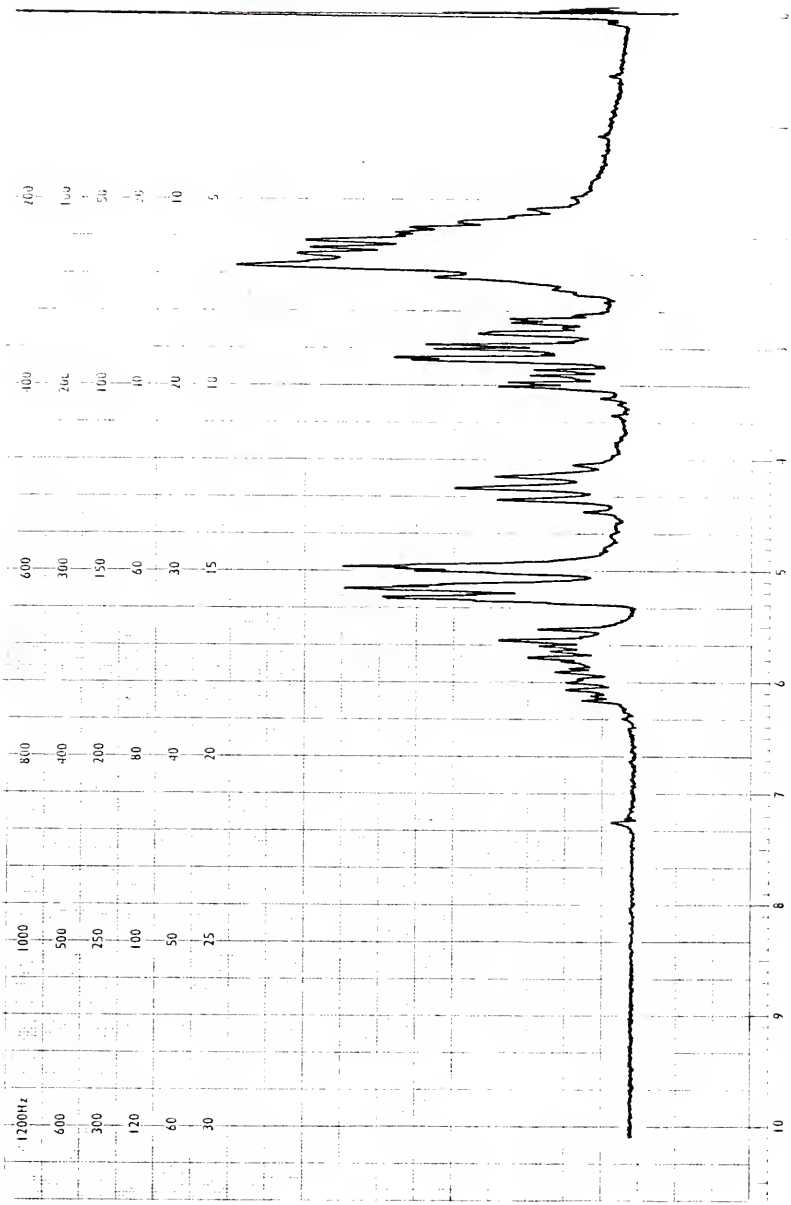


Figure 11. ^{1}H NMR of 5,7-Dibromo-7,7-difluoro-1-heptene, 19.

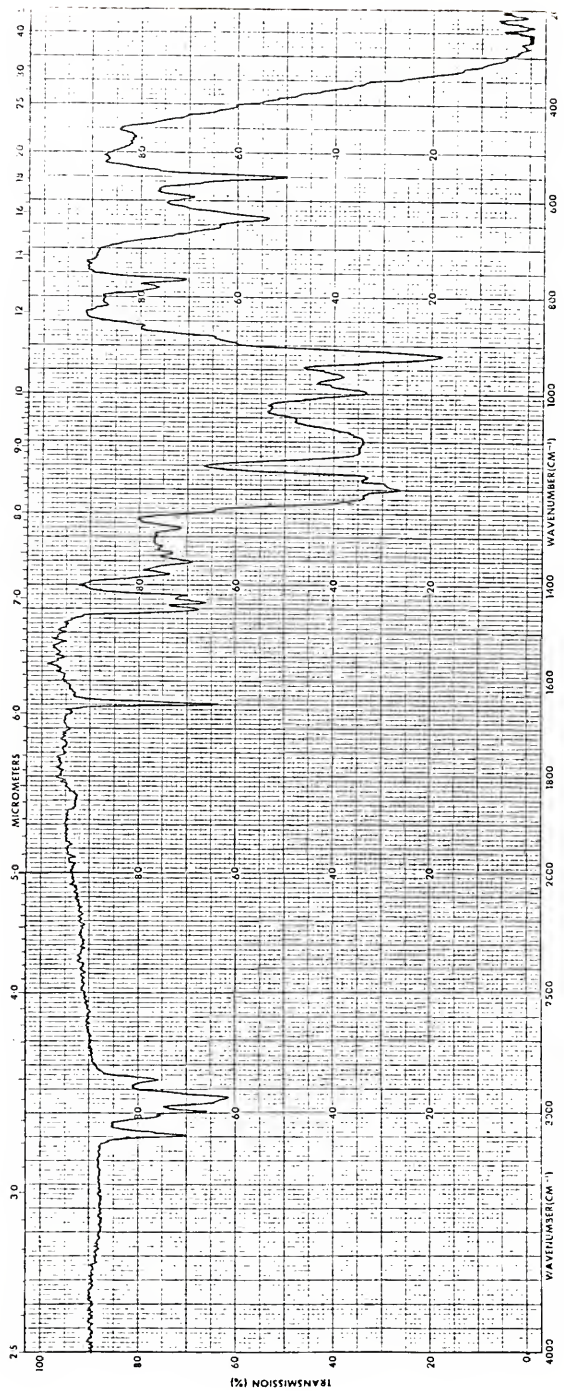


Figure 12. IR of 5,7-Dibromo-7,7-difluoro-1-heptene, 19.

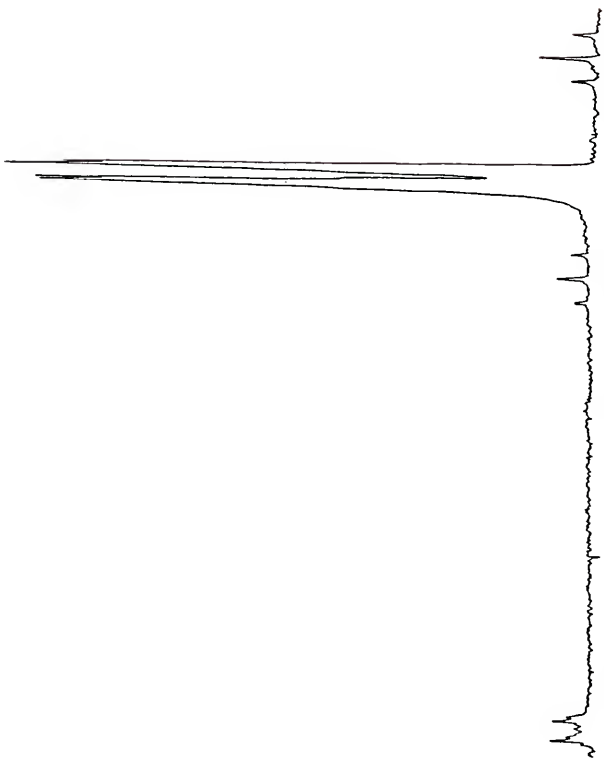


Figure 13. ^{19}F NMR of 7-Bromo-7,7-difluoro-1,5-heptadiene, 20c at ϕ 39.3 ppm, 20t at ϕ 44.6 ppm.

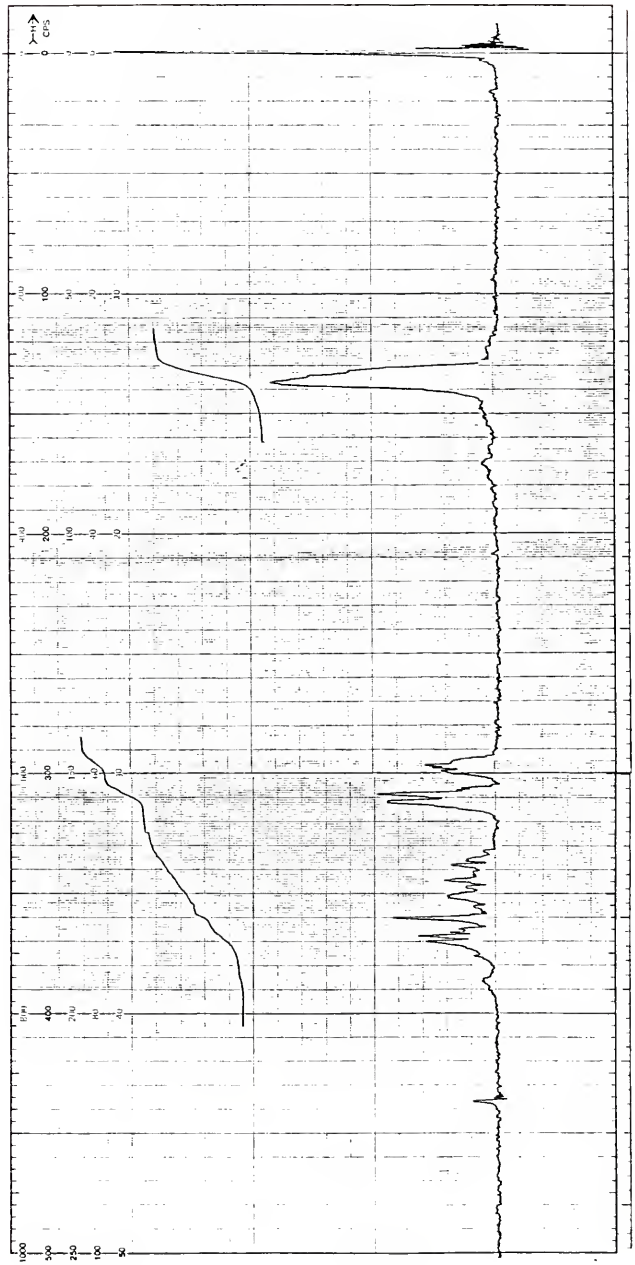


Figure 14. ^{1}H NMR of 7-Bromo-7,7-difluoro-1,5-heptadiene, 20c and 20t.

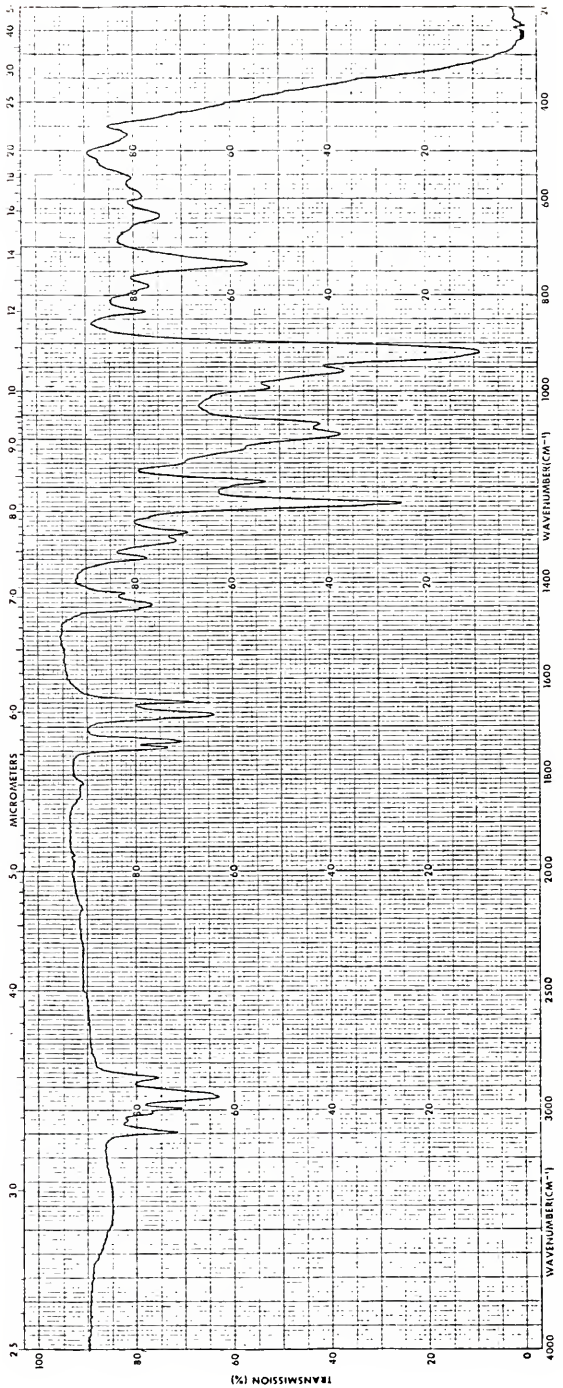


Figure 15. IR of 7-Bromo-7,7-difluoro-1,5-heptadiene, 20c and 20t.

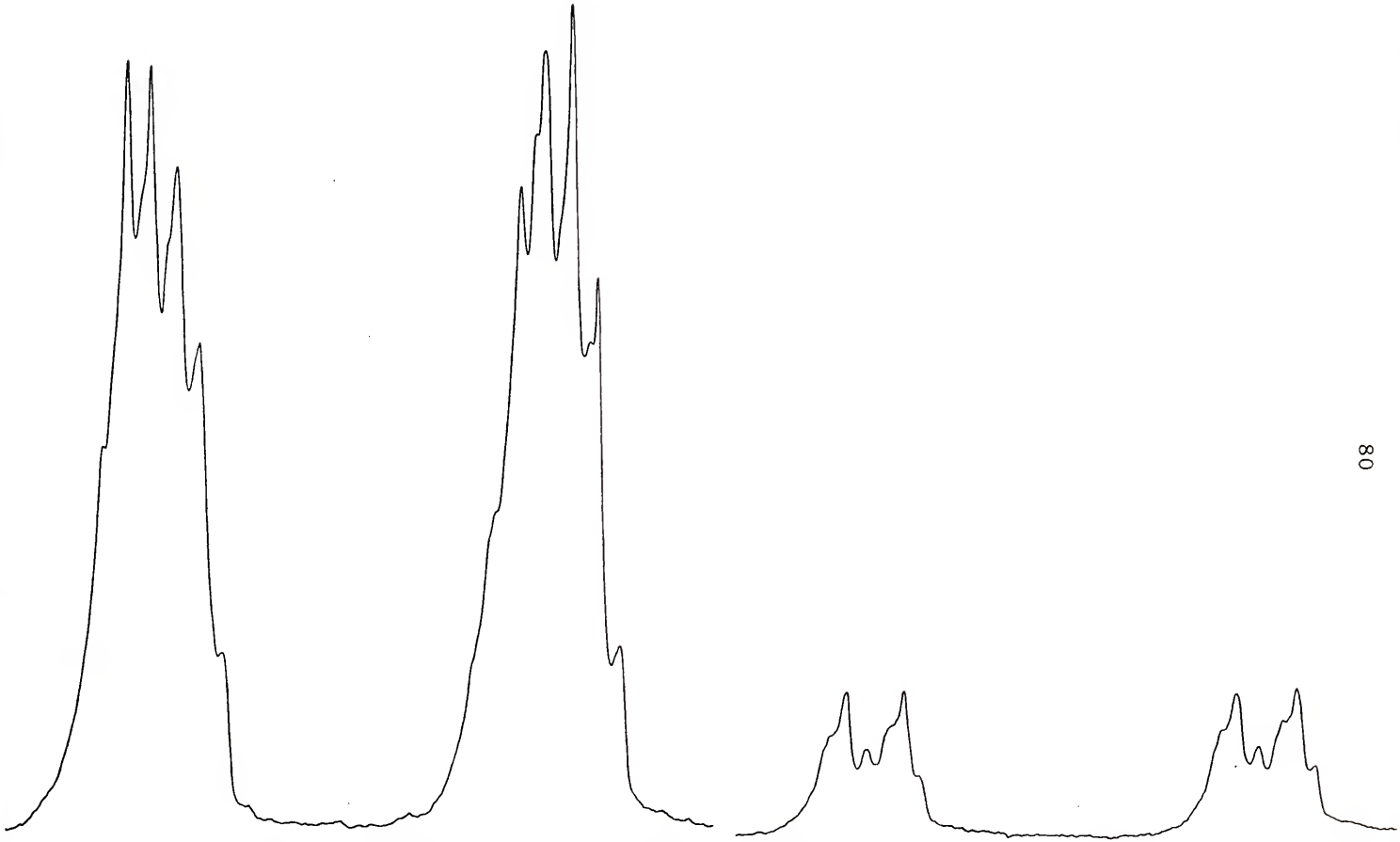


Figure 16. ^{19}F NMR of 7,7-Difluoro-1,5-heptadiene, 21c at ϕ 111.4 ppm, 21t at ϕ 110.3 ppm.

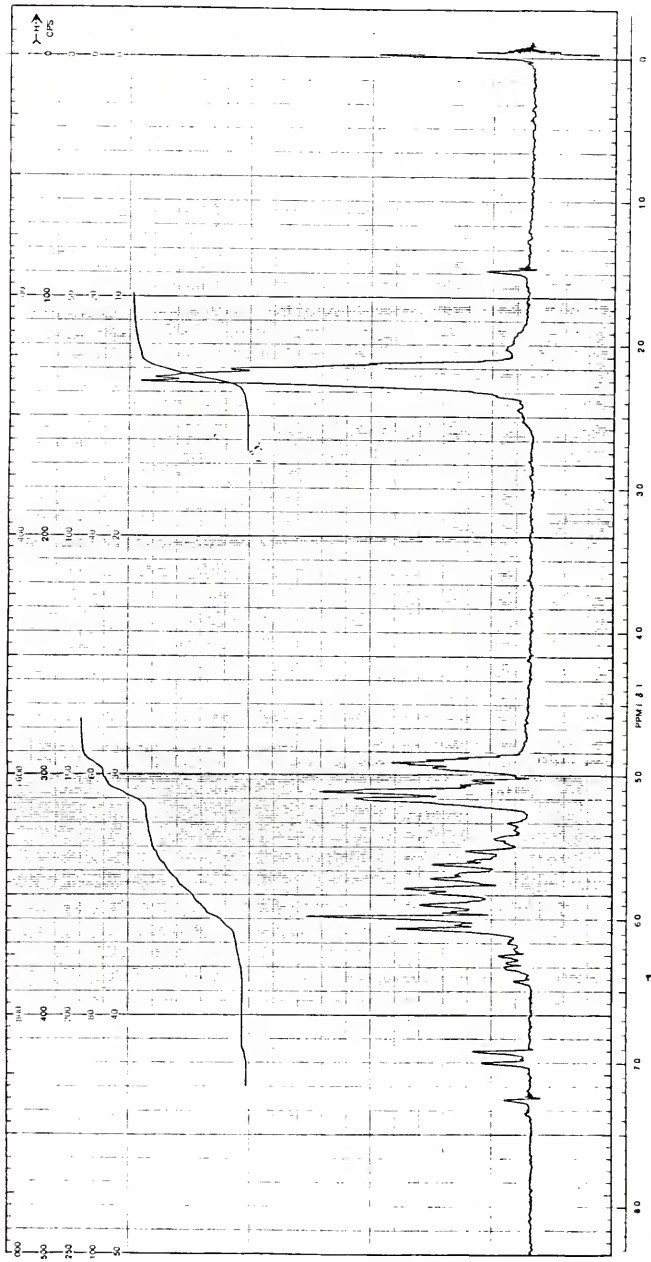


Figure 17. ^{1}H NMR of 7,7-Difluoro-1,5-heptadiene, 21c and 21t.

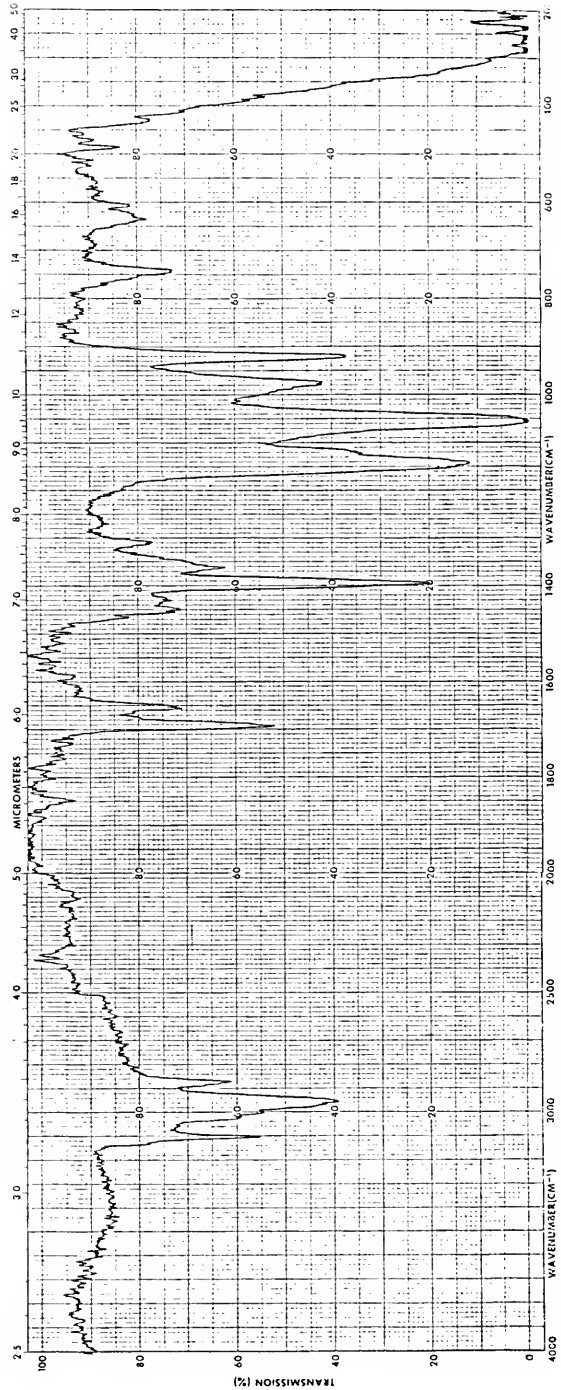


Figure 18. IR of 7,7-Difluoro-1,5-heptadiene, 21c and 21t.

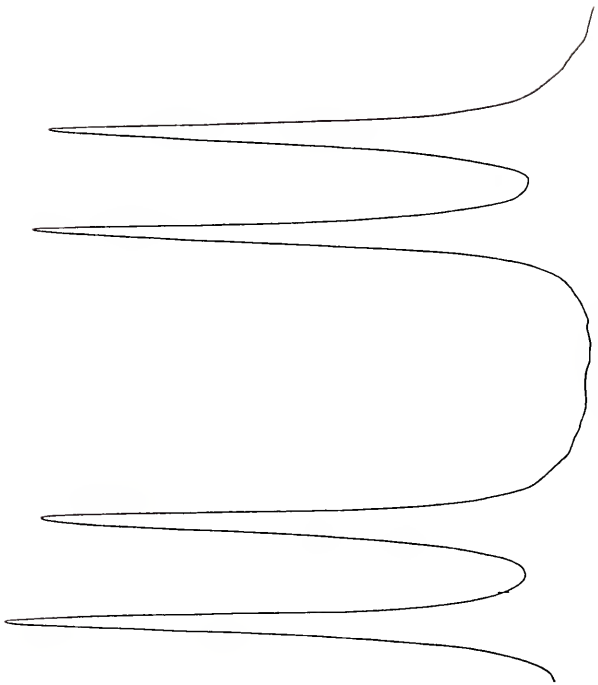


Figure 19. ^{19}F NMR of 3-Difluoromethyl-1,5-hexadiene, 22.

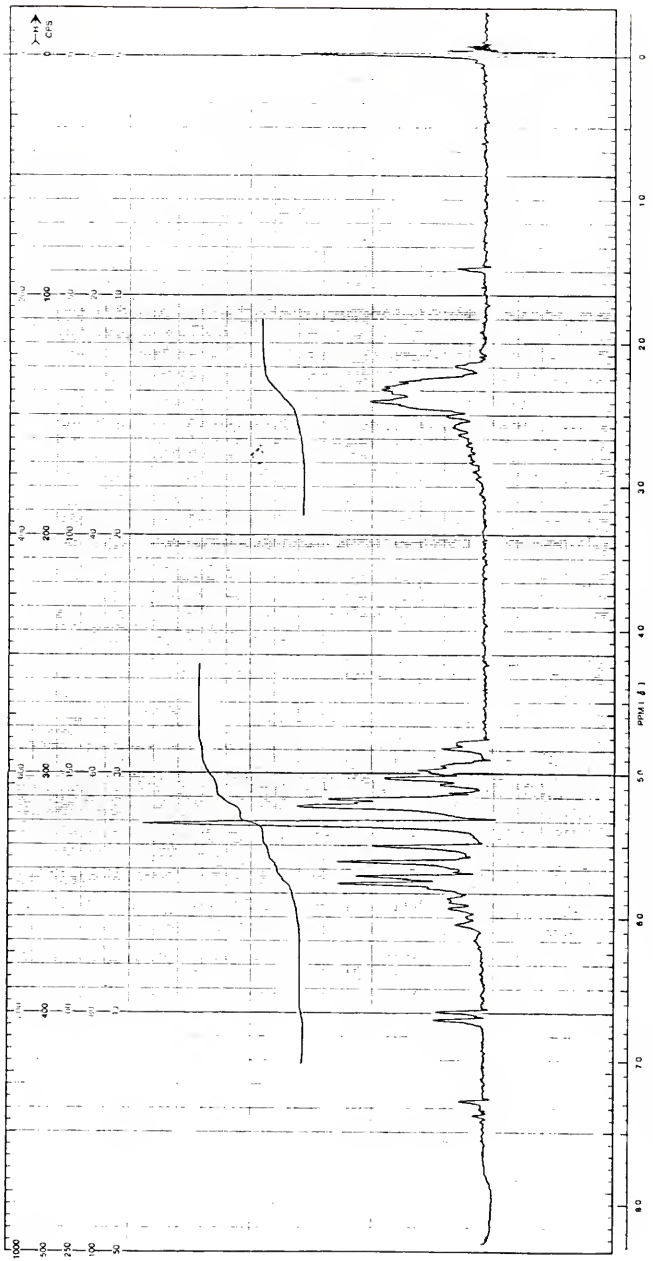


Figure 20. ^{1}H NMR of 3-Difluoromethyl-1,5-hexadiene, 22.

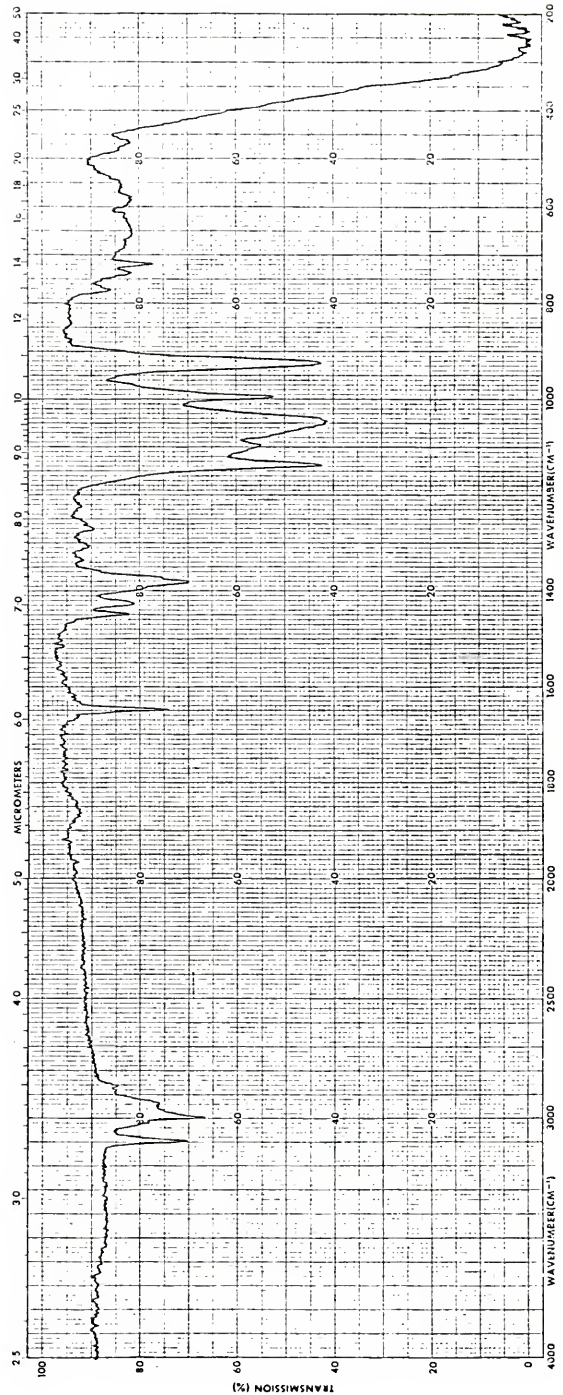


Figure 21. IR of 3-Difluoromethyl-1,5-hexadiene, 22.

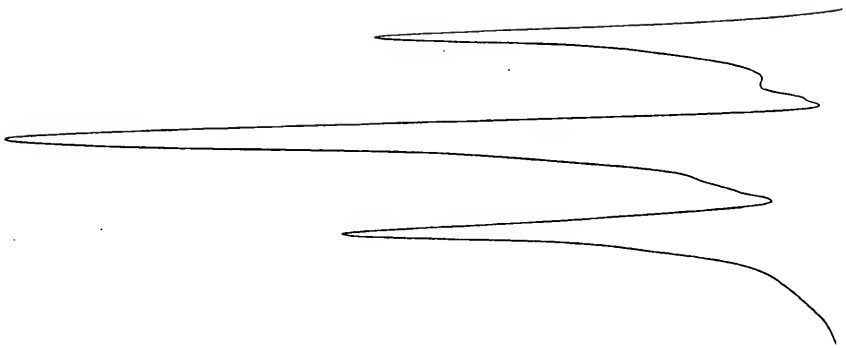


Figure 22. ^{19}F NMR of 5-Iodo-7,7,7-trifluoro-1-heptene, 23, ϕ 64.4 ppm.

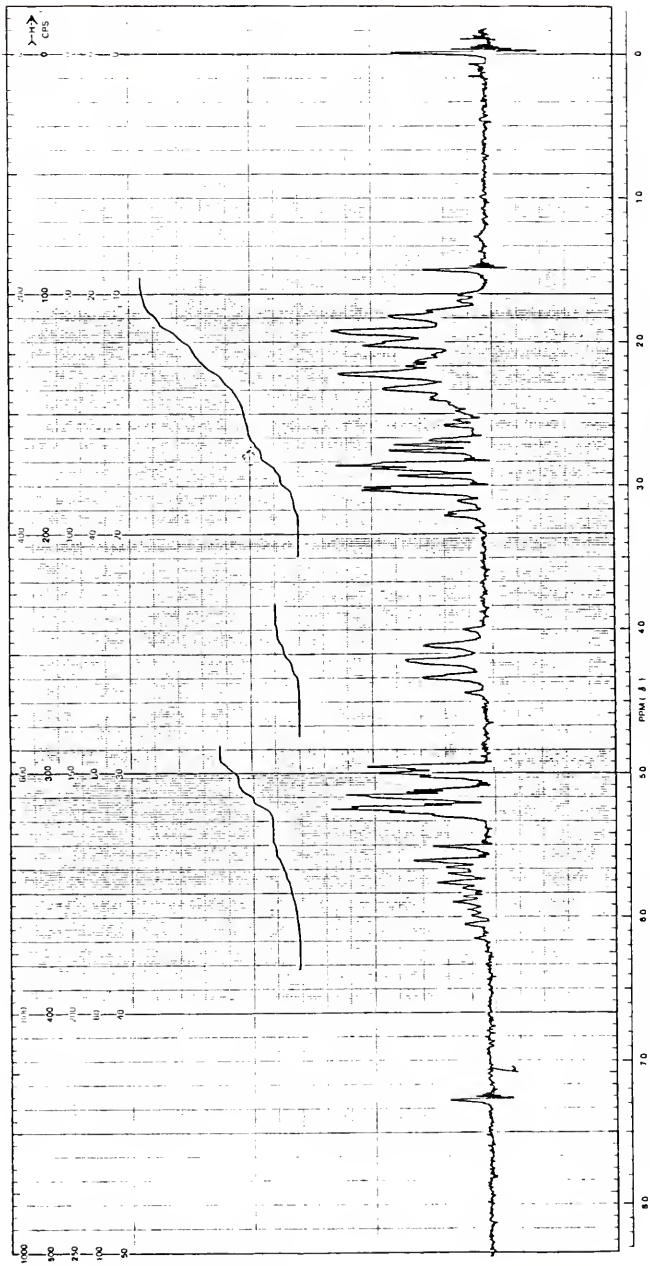


Figure 23. ^{1}H NMR of 5-Iodo-7,7,7-trifluoro-1-heptene, 23.

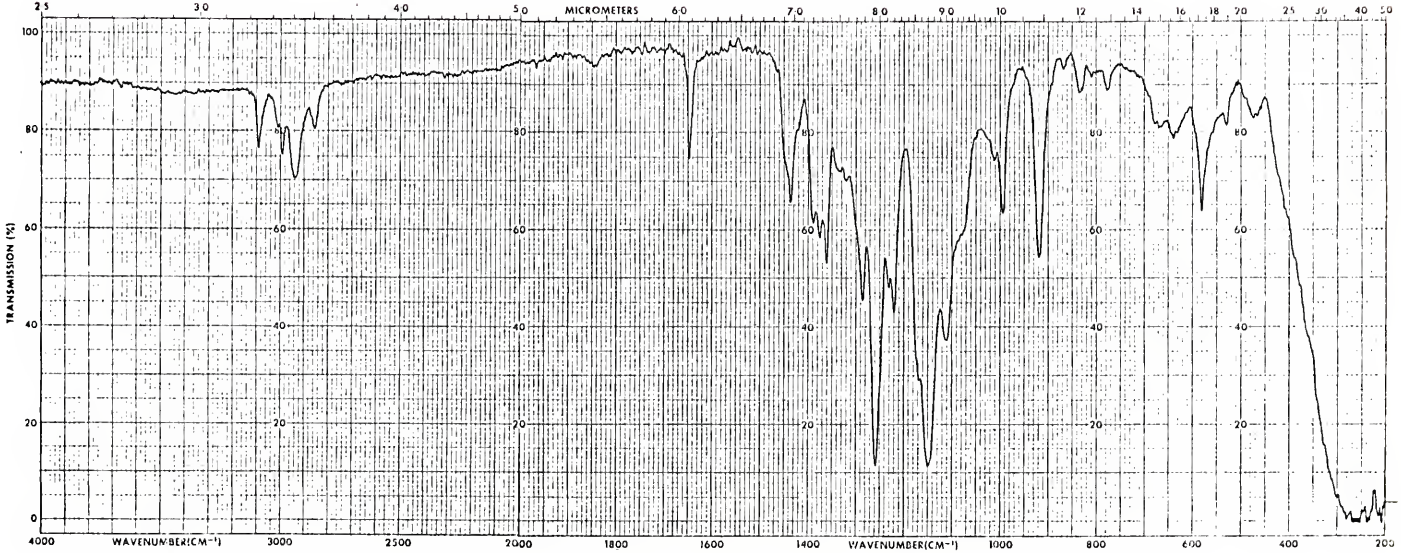


Figure 24. IR of 5-Iodo-7,7,7-trifluoro-1-heptene, 23.

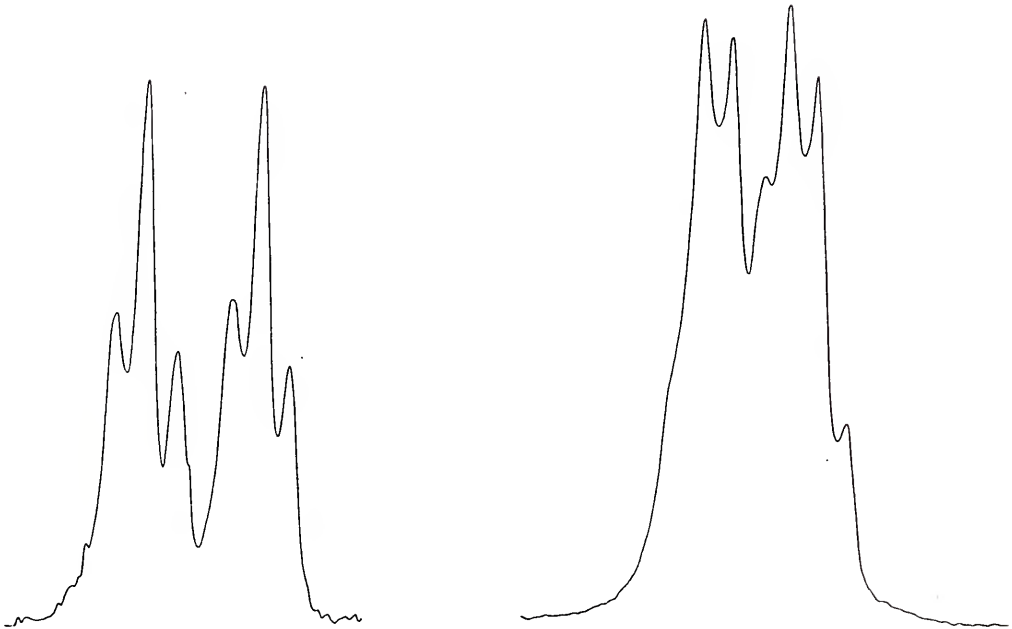


Figure 25. ^{19}F NMR of 7,7,7-Trifluoro-1,5-heptadiene, 24c at ϕ 58.9 ppm, 24t at ϕ 64.6 ppm.

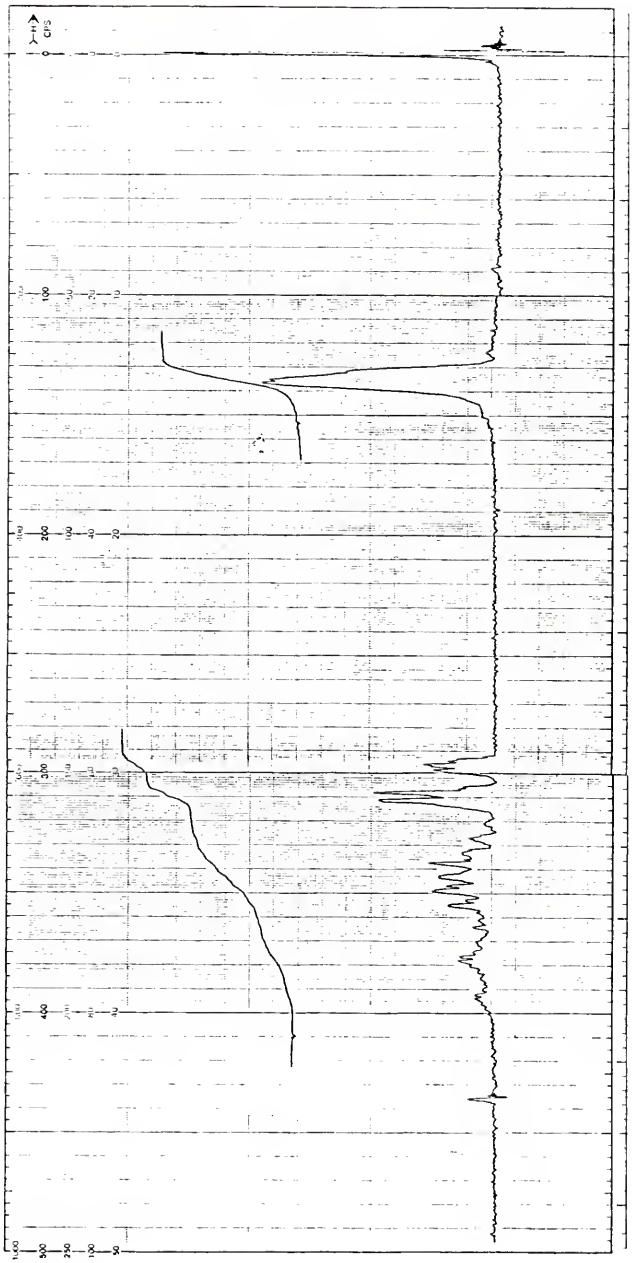


Figure 26. ^{1}H NMR of 7,7,7-Trifluoro-1,5-heptadiene, 24t and 24c.

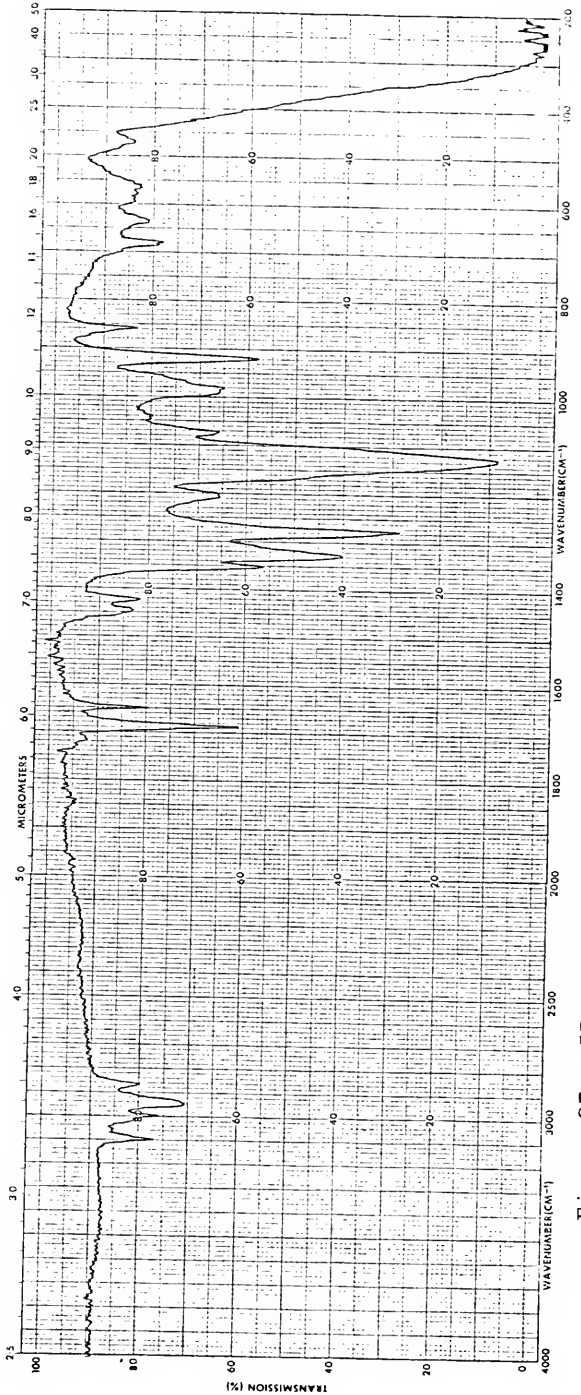


Figure 27. IR of 7,7,7-Trifluoro-1,5-heptadiene, 24t and 24c.

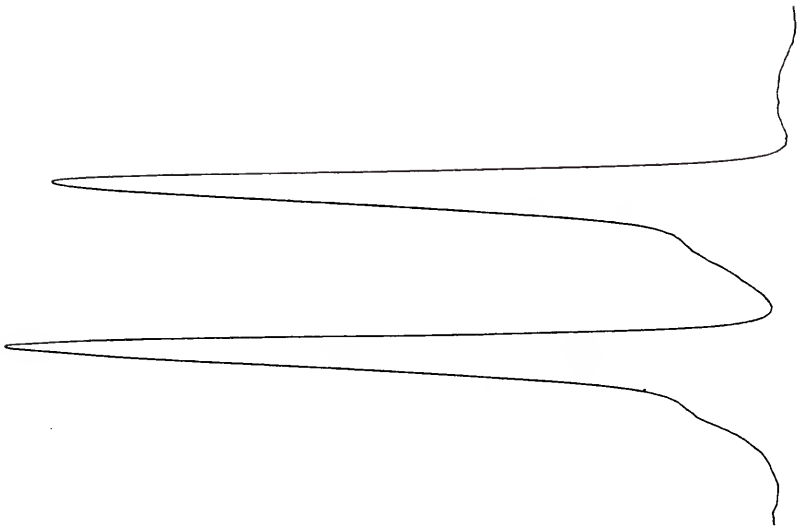


Figure 28. ^{19}F NMR of 3-Trifluoro-1,5-hexadiene, 25, ϕ 71.5 ppm.

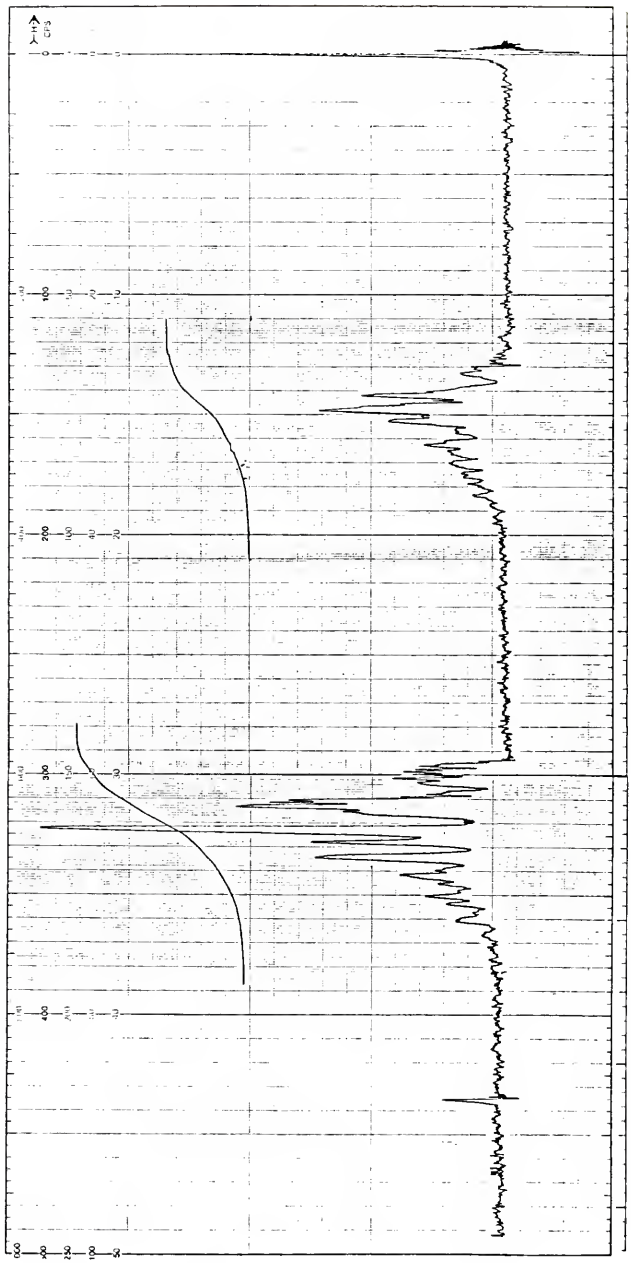


Figure 29. ^{1}H NMR of 3-Trifluoro-1,5-hexadiene, 25.

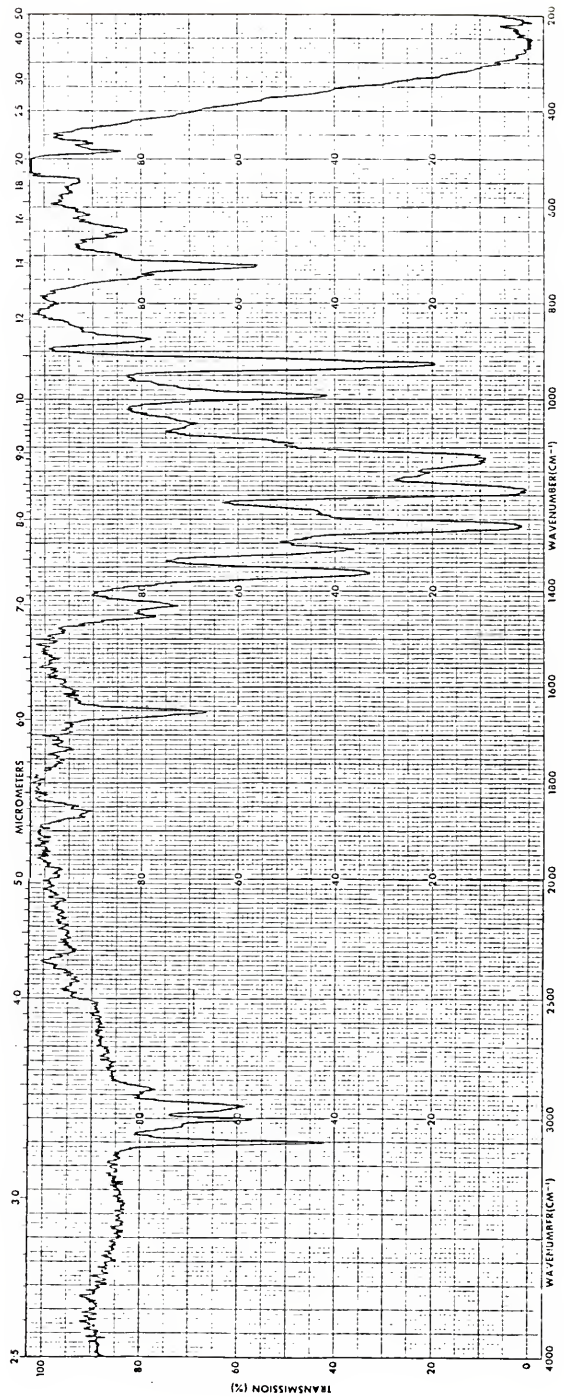


Figure 30. IR of 3-Trifluoro-1,5-hexadiene, 25.

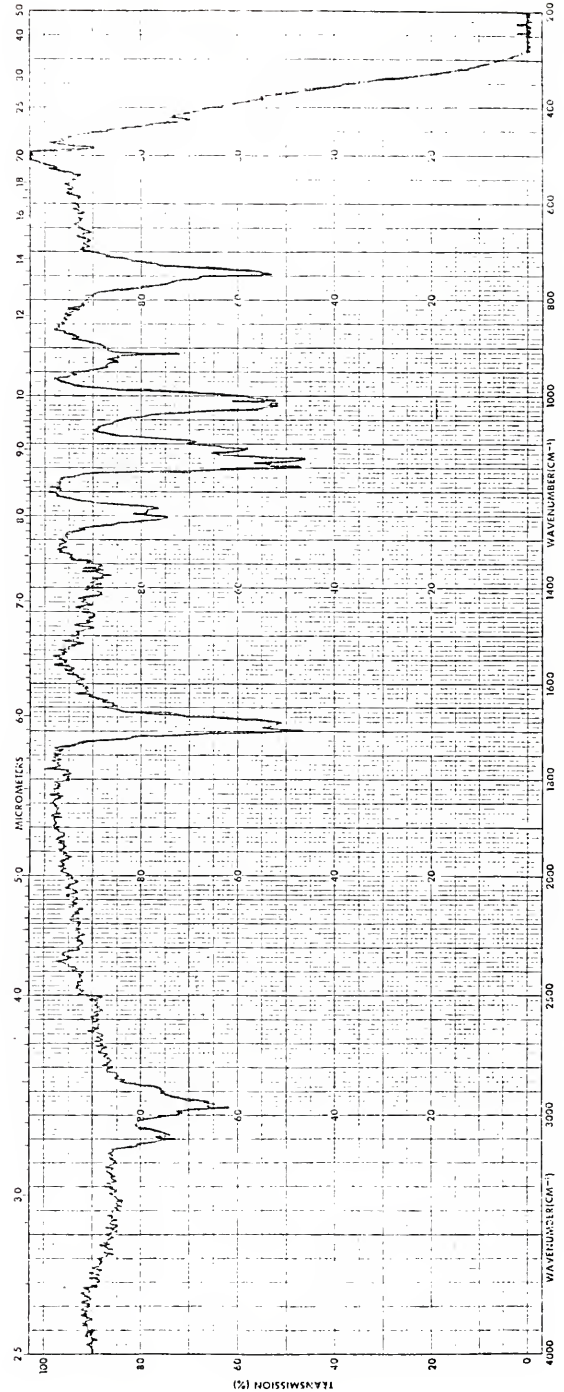


Figure 31. IR of 1-Fluoropropene, 27c and 27t.

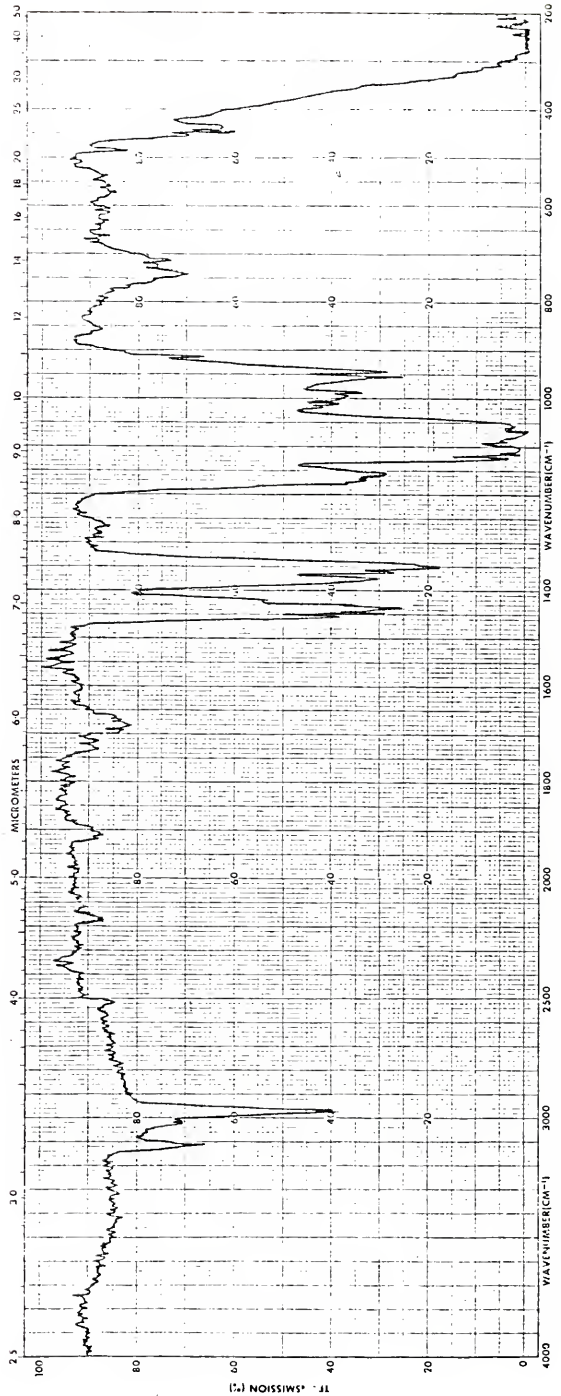


Figure 32. IR of 3,3-Difluoropropene, 28.

APPENDIX 2
KINETIC AND THERMODYNAMIC DATA

TABLE 1. RATE DATA FOR 17 → 18

Run Number	Temperature	Time (sec)	17/18
1	194.3°	3600	7.31
		6180	4.78
		9000	3.43
		12000	2.83
		15000	2.20
		18000	1.77
		21000	1.46
		25500	1.14
		∞	0.00755

$k = 0.0000227 \pm 0.0000004\ sec^{-1}$

corr. coeff. = 0.99889

Run Number	Temperature	Time (sec)	17/18
2	198.4°	3000	8.98
		6300	4.15
		9000	2.81
		15000	1.54
		18000	1.22
		21000	1.01
		24000	0.828
		∞	0.00434

TABLE 1—Continued

$k = 0.0000326 \pm 0.0000002\ sec^{-1}$

corr. coeff. = 0.99996

Run Number	Temperature	Time (sec)	17/18
3	202.4°	2400	8.48
		3660	5.16
		5100	3.82
		6600	2.74
		7800	2.36
		10380	1.68
		12900	1.27
		15780	0.971
		∞	0.00599

$k = 0.0000443 \pm 0.0000004\ sec^{-1}$

corr. coeff. = 0.99974

Run Number	Temperature	Time (sec)	17/18
4	206.8°	2460	6.23
		3480	4.25
		4980	2.92
		6060	2.30
		6960	1.98
		8340	1.59
		10200	1.22

TABLE 1—Continued

Run Number	Temperature	Time (sec)	17/18
		12000	0.980
		∞	0.00572

$k = 0.0000581 \pm 0.0000002\ sec^{-1}$

corr. coeff. = 0.99993

Run Number	Temperature	Time (sec)	17/18
5	210.7°	1260	9.34
		2100	5.37
		3420	3.22
		4500	2.33
		5880	1.71
		6960	1.37
		8280	1.10
		9840	0.870
		∞	0.00485

$k = 0.0000775 \pm 0.0000003\ sec^{-1}$

corr. coeff. = 0.99997

Run Number	Temperature	Time (sec)	17/18
6	214.6°	1200	6.96
		1800	4.78

TABLE 1—Continued

Run Number	Temperature	Time (sec)	17/18
		3060	2.59
		4200	1.83
		5220	1.38
		6120	1.14
		7740	0.816
		8160	0.768
		∞	0.00410

$k = 0.0001015 \pm 0.0000006\ sec^{-1}$

corr. coeff. = 0.99991

TABLE 2. ARRHENIUS PARAMETERS FOR 17 → 18

Temperature	k (sec^{-1})	corr. coeff.
194.3°	0.0000227 ± 0.0000004	0.99889
198.4°	0.0000326 ± 0.0000002	0.99996
202.4°	0.0000443 ± 0.0000004	0.99974
206.8°	0.0000581 ± 0.0000002	0.99993
210.7°	0.0000775 ± 0.0000003	0.99997
214.6°	0.0001015 ± 0.0000006	0.99991

E_a = 33.0 ± 0.7 kcal/mole

Log A = 10.8 ± 0.3 sec^{-1}

corr. coeff. = 0.999

$\Delta H^{\ddagger}$ = 32.0 kcal/mole

$\Delta S^{\ddagger}$ = -12.2 e.u.

$\Delta G^{\ddagger}$ = 37.8 kcal/mole

TABLE 3. EQUILIBRIUM CONSTANTS FOR 22 ⇌ 21c ⇌ 21t

Temperature	Start. Mat.(10 mm)	22/21c	22/21t	21c/21t
409.0°	21c and 21t	2.18	0.460	0.211
409.0°	22	2.19	0.464	0.211
394.8°	22	2.21	0.455	0.206
381.8°	22	2.23	0.448	0.201
370.0°	22	2.25	0.446	0.198
356.4°	22	2.27	0.436	0.192
345.0°	22	2.29	0.433	0.189
332.2°	22	2.31	0.427	0.185
321.2°	22	2.33	0.424	0.182
309.9°	22	2.35	0.418	0.178

TABLE 4. ENTHALPY AND ENTROPY FOR 22 ⇌ 21c ⇌ 21t

21c ⇌ 22

$\Delta H = -0.563 \pm 0.006$ kcal/mole

$\Delta S = 0.733 \pm 0.002$ e.u.

corr. coeff. = 0.999

21t ⇌ 22

$\Delta H = 0.80 \pm 0.04$ kcal/mole

$\Delta S = -0.36 \pm 0.01$ e.u.

corr. coeff. = 0.993

21t ⇌ 21c

$\Delta H = 1.37 \pm 0.04$ kcal/mole

$\Delta S = -1.09 \pm 0.01$ e.u.

corr. coeff. = 0.997

TABLE 5. EQUILIBRIUM CONSTANTS FOR 25 $\rightleftharpoons$ 24c $\rightleftharpoons$ 24t

Temperature	Start. Mat. (10 mm)	$K_{25/24c}$	$K_{24c/24t}$	$K_{25/24t}$
408.0°	24c and 24t	2.26	0.172	0.389
408.0°	25	2.28	0.172	0.392
394.4°	25	2.34	0.168	0.393
380.9°	25	2.42	0.161	0.390
368.7°	25	2.47	0.157	0.388
356.3°	25	2.49	0.154	0.383
344.6°	25	2.55	0.152	0.387
332.5°	25	2.61	0.147	0.384
321.3°	25	2.70	0.144	0.384

TABLE 6. ENTHALPY AND ENTROPY FOR 25 ⇌ 24c ⇌ 24t

24c ⇌ 25

$\Delta H = -1.47 \pm 0.07$ kcal/mole

$\Delta S = -0.51 \pm 0.02$ e.u.

corr. coeff. = 0.993

24t ⇌ 25

$\Delta H = 0.23 \pm 0.05$ kcal/mole

$\Delta S = -1.52 \pm 0.02$ e.u.

corr. coeff. = 0.877

24t ⇌ 24c

$\Delta H = 1.63 \pm 0.08$ kcal/mole

$\Delta S = -1.12 \pm 0.02$ e.u.

corr. coeff. = 0.992

TABLE 7. EQUILIBRIUM CONSTANTS FOR 27c ⇌ 27t ⇌ 26

Temperature	Start. Mat.	$K_{27c/27t}$	$K_{27c/26}$	$K_{27t/26}$
312°[a]	90 mm 26	1.92	10.2	5.29
	110 mm 26	1.91	9.06	4.74
	100 mm 26	1.92	8.83	4.60
	65 mm 26	1.91	9.28	4.86
343.9°	110 mm 26	1.95	7.53	3.85
	105 mm 26	1.96	7.65	3.91
	90 mm 26	1.95	7.43	3.82
	130 mm 26	1.94	7.56	3.89
356.0°	110 mm 26	1.97	7.29	3.68
	90 mm 26	1.97	7.23	3.65
	110 mm 26	1.96	7.15	3.69
	90 mm 26	1.94	7.18	3.69
380.5°[b]		1.90	6.51	3.43
398.0°[b]		1.90	6.10	3.21
415.0°[b]		1.85	5.66	3.07
430.3°	110 mm 26	1.84	5.44	2.98
	110 mm 27	1.83	5.45	2.96
	85 mm 27	1.85	5.49	2.97

[a] Data obtained at this temperature was not used in the van't Hoff plots.

[b] Average of two runs per temperature.

TABLE 8. ENTHALPY AND ENTROPY FOR 27c ⇌ 27t ⇌ 26

27t ⇌ 27c

$\Delta H = -0.64 \pm 0.09$ kcal/mole

$\Delta S = 0.30 \pm 0.03$ e.u.

corr. coeff. = 0.963

26 ⇌ 27c

$\Delta H = -3.34 \pm 0.07$ kcal/mole

$\Delta S = -1.39 \pm 0.02$ e.u.

corr. coeff. = 0.9991

26 ⇌ 27t

$\Delta H = -2.68 \pm 0.07$ kcal/mole

$\Delta S = -1.70 \pm 0.02$ e.u.

corr. coeff. = 0.9988

TABLE 9. EQUILIBRIUM CONSTANTS FOR 29 ⇌ 28

Temperature	Start. Mat.	$K_{28/29}$
412.8°	40 mm 28	5.35
412.8°	60 mm 28	5.42
412.5°	50 mm 29	5.34
412.5°	40 mm 28	5.38
412.5°	60 mm 28	5.38
405.5°	a	5.48
399.0°	a	5.60
391.5°	a	5.68
384.8°	a	5.79
378.3°	a	5.96

a. Average of two runs.

TABLE 10. ENTHALPY AND ENTROPY FOR 29 $\rightleftharpoons$ 28

29 $\rightleftharpoons$ 28

$\Delta H = -2.5 \pm 0.1$ kcal/mole

$\Delta S = -0.38 \pm 0.04$ e.u.

corr. coeff. = 0.9948

REFERENCES

1. R. D. Chambers, "Fluorine in Organic Chemistry," Wiley-Interscience, New York, N.Y., 1973.

2. C. R. Patrick, Adv. in Fluorine Chemistry, 2, 1(1961).

3. K. W. Egger and A. T. Cocks, Helv. Chim. Acta, 56, 1516(1973).

4. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," John Wiley and Sons, Inc., New York, N.Y., 1969.

5. L. Pauling, "Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, Ithaca, N.Y., 1960, pp. 88-102.

6. L. Radom, W. J. Hehre, and J. A. Pople, J. Amer. Chem. Soc., 93, 289(1971).

7. L. Radom and P. J. Stiles, Tetrahedron Letters, 789 (1975).

8. H. A. Bent, Chemical Reviews, 61, 275(1961).

9. W. A. Bernett, J. of Organic Chemistry, 34 1772(1969).

10. A. S. Rodgers and W. C. F. Ford, Int. J. of Chemical Kinetics, 5, 965(1973).

11. R. W. Carr, Jr., and W. D. Walters, J. of Physical Chemistry, 67, 1370(1963).

12. R. T. Conlin and H. M. Frey, J. C. S. Faraday Trans. I, 75, 2556(1979).

13. R. T. Conlin and H. M. Frey, J. C. S. Faraday Trans. I, 76, 322(1980).

14. J. N. Butler, J. Amer. Chem. Soc., 84, 1393(1962).

15. D. Peters, J. of Chemical Physics, 38, 561(1963).

16. B. E. Smart, personal communication.

17. V. W. Laurie and D. T. Pence, J. Chemical Physics, 38, 2693(1963).

18. J. L. Carlos, Jr., R. R. Karl, Jr., and S. H. Bauer, J. C. S. Faraday Trans. II, 70, 177(1974).

19. J. M. Pickard and A. S. Rodgers, J. Amer. Chem. Soc. 99, 695(1977).

20. J. R. Lacher and H. A. Skinner, J. of the Chemical Society A, 1034(1968).

21. J. A. Sell and A. Kupperman, J. of Chemical Physics, 71, 4703(1979).

22. P. Mollere, H. Bock, G. Becker, and G. Fritz, J. of Organometallic Chemistry, 46, 89(1972).

23. G. W. Mines and H. W. Thompson, Spectrochimica Acta A, 29A, 1377(1973).

24. C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Busch, J. Amer. Chem. Soc., 94, 1451(1972).

25. E. Hirota, J. of Chemical Physics, 37, 283(1962).

26. P. I. Abell and P. K. Adolf, J. of Chemical Thermodynamics, 1, 333(1969).

27. A. Liberles, A. Greenberg, and J. E. Eilers, J. of Chemical Education, 50, 676(1973).

28. R. C. Bingham, J. Amer. Chem. Soc., 98, 535(1976).

29. J. P. Chesick, J. Amer. Chem. Soc., 88, 4800(1966).

30. E. W. Schlag and W. B. Peatman, J. Amer. Chem. Soc., 86, 1976(1964).

31. H. M. Frey, R. G. Hopkins, and I. C. Vinall, J. C. S. Faraday Trans. I, 68, 1874(1972).

32. Z. B. Alfassi, D. M. Golden, and S. W. Benson, J. Chemical Thermodynamics, 5, 411(1973).

33. W. R. Dolbier, Jr., C. A. Piedrahita, and B. H. Al-Sader, Tetrahedron Letters, 2957(1979).

34. S. Sellers and W. R. Dolbier, Jr., unpublished results.

35. H. M. Frey and R. K. Solly, Trans. Faraday Society, 65, 1372(1969).

36. M. R. Willcott, R. L. Cargill, and A. B. Sears in "Progress in Physical Organic Chemistry," (A. Streitwieser, Jr., and R. W. Taft, eds.), 9, 25-98. Wiley-Interscience, New York, N.Y., 1972.

37. S. W. Benson, A. N. Bose, and P. Nangia, J. Amer. Chem. Soc., 85, 1388(1963).

38. L. N. Markovskij, V. E. Pashinnik, and A. V. Kirsanov, Synthesis, 787(1973).

39. L. K. Montgomery and J. W. Matt, J. Amer. Chem. Soc., 89, 6556(1967).

40. D. G. Naae and D. J. Burton, Synthetic Communications, 3, 197(1973).

41. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley and Sons, Inc., New York, N.Y., p. 1192.

42. R. Gregory, R. N. Haszeldine, and A. E. Tipping, J. Chem. Soc. (C), 1216(1971).

43. F. W. Hoffman, J. of Organic Chemistry, 15, 425(1950).

44. A. A. Bothner-By, S. Catellano, and H. Gunther, J. of Amer. Chem. Soc., 87, 2439(1965).

45. "Sadtler Standard Spectra," Coblentz Society Spectra, 9, 8840.

46. R. A. Beaudet and J. D. Baldeschwieler, J. Molecular Spectroscopy, 9, 30(1962).

47. S. J. Moss and K. R. Jennings, Transactions Faraday Society, 65, 415(1969).

48. V. W. Weiss, P. Beak, and W. H. Flygare, J. Chemical Physics, 46, 981(1967).

49. S. W. Benson, "Thermochemical Kinetics," 2nd Ed., Wiley-Interscience, New York, N.Y., 1976.

50. S. S. Chen, A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinsky, J. Phys. Chem. Ref. Data, 4, 441(1975).

51. J. B. Pedley and J. Rylance, "Sussex-N. P. L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds," Sussex University, Brighton, G.B.

52. A. Greenberg, personal communication.

53. C. W. Bock, P. George, G. J. Mains, and M. Trachtman, J. C. S. Parkin II, 814(1979).

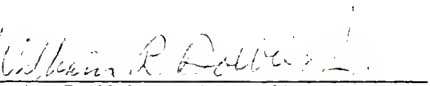
54. J. D. Dill, A. Greenberg, and J. F. Liebman, J. Amer. Chem. Soc., 101, 6814(1979).

BIOGRAPHICAL SKETCH

Karl S. Medinger was born December 16, 1953, in Coatesville, Pennsylvania. When he was 12, he made his first motorcycle from used parts and riding became a lifetime hobby. He graduated from Coatesville Area High School in June 1972, and entered University of Pittsburgh, September 1972. There he met Sue-Ellen Weir, lived with her for two years and married in August 1975. The following year, on July 12, 1976, his daughter, Selena, was born. In August he moved with his family to Gainesville, Florida, and began a five year career at the University of Florida as a chemistry graduate student. He continued to pursue his hobby of motorcycle riding, entering trials competition in the state of Florida. He achieved Expert ranking in September of 1980, and was ranked 9th in the state.

In May 1981, he received a job offer from Union Carbide in Charleston, West Virginia. He and his family, along with two cats and a motorcycle, will move there in September 1981.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

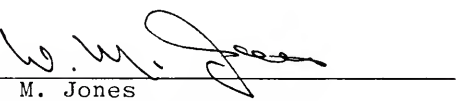


W. R. Dolbier, Jr., Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

M. A. Battiste
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



W. M. Jones
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

G. M. Schmid
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

W. H. Cutler
Associate Professor of Speech

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1981

Dean, Graduate Studies
and Research

UNIVERSITY OF FLORIDA
3 1262 08553 1845